Modern advances in bismaleimide resin technology: a 21st century perspective on the chemistry of addition polyimides

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This review is respectfully and affectionately dedicated to Dr Horst D Stenzenberger, who has been an inspirational figure in modern BMI chemistry, always happy to share his extensive knowledge of this field.

ABSTRACT: The chemistry of bismaleimides (BMIs), their blends and copolymers is reviewed critically with particular emphasis placed on the development of the field after 1990, which was marked by several comprehensive review articles. A general introduction to the structure property relationships of BMIs is presented, outlining the development of the preparative chemistry, and the early strategies adopted to address the inherent brittleness of the cured 'first generation' BMI polymers. 'Second generation', diallylbisphenol-toughened BMIs, form the basis of the benchmark commercial systems, and the polymerization mechanism is discussed. The current review is placed in context, addressing the issues of cost, processing and precursor toxicity, the major barriers to wider acceptance of BMIs. The main body of the review evaluates a number of observations made by Dr Horst Stenzenberger in 1990, for the future development of BMI technology. Hence, the synthesis of novel bismaleimide building blocks, incorporation of new thermoplastics and additives, and blending with new thermosetting comonomers are all discussed in detail. The aforementioned review had been written before the concept of nanocomposites or shape memory polymers had been explored with BMIs, but the fields have since grown (especially in the case of the former topic) and are reviewed herein. The application of BMIs to continuous fibre composites is one of the proposed fields of commercial development. The topic falls a little beyond the scope of the present review of BMI chemistry, and is the subject of another publication, but a brief discussion of the most recent developments is presented. The review is concluded with some thoughts about the future outlook for BMI chemistry.

Keywords: Bismaleimide Chemistry, Thermoset Blends, Thermoplastic Toughening, Nanocomposites, Shape Memory Polymers, Continuous Fibre Composites.

1. INTRODUCTION TO BMI CHEMISTRY

Bismaleimide (BMI) resins are a family of high performance thermosetting polymers that possess a range of attractive properties for industrial applications, particularly in the aerospace materials sector. BMI monomers (the general structure is outlined in Figure 1) are molecules that are terminated by two maleimide functional groups, often containing multiple aromatic moieties in order to enhance their cured properties. Typical properties associated with cured BMI systems include high (dry) glass transition temperatures (230 – 380 °C), good hot-wet performance, constant electrical properties and low flammability (Table 1).

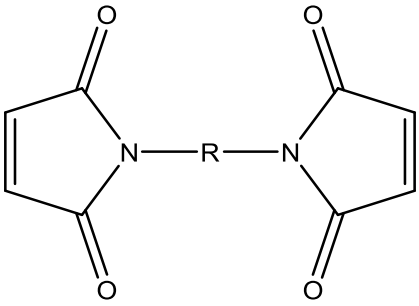


Figure 1: General structure of a bismaleimide monomer, R = alkyl or aryl.

Table 1 Typical cured BMI properties (shown for bis(4-maleimidophenyl)methane a first generation, untoughened BMI, [1])

Property	**Cured BMI value**
Colour	Brown
Glass transition temperature (°C)	342
Tensile strength (MPa)	40-80
Tensile modulus (GPa)	4.1-4.8
Fracture energy (J m^{-2})	25-34

Since the initial synthesis of difunctional monomers in 1975 by D'Alelio [2], the technology of these systems has developed significantly to the point that BMI resins are now leading contenders in the field of advanced thermosets. It is clear from Figure 2, that BMIs occupy a specific niche in the high performance polymer spectrum, combining some of the high temperature properties of thermosetting polyimides with the facile processability of the industry standard epoxy resins.

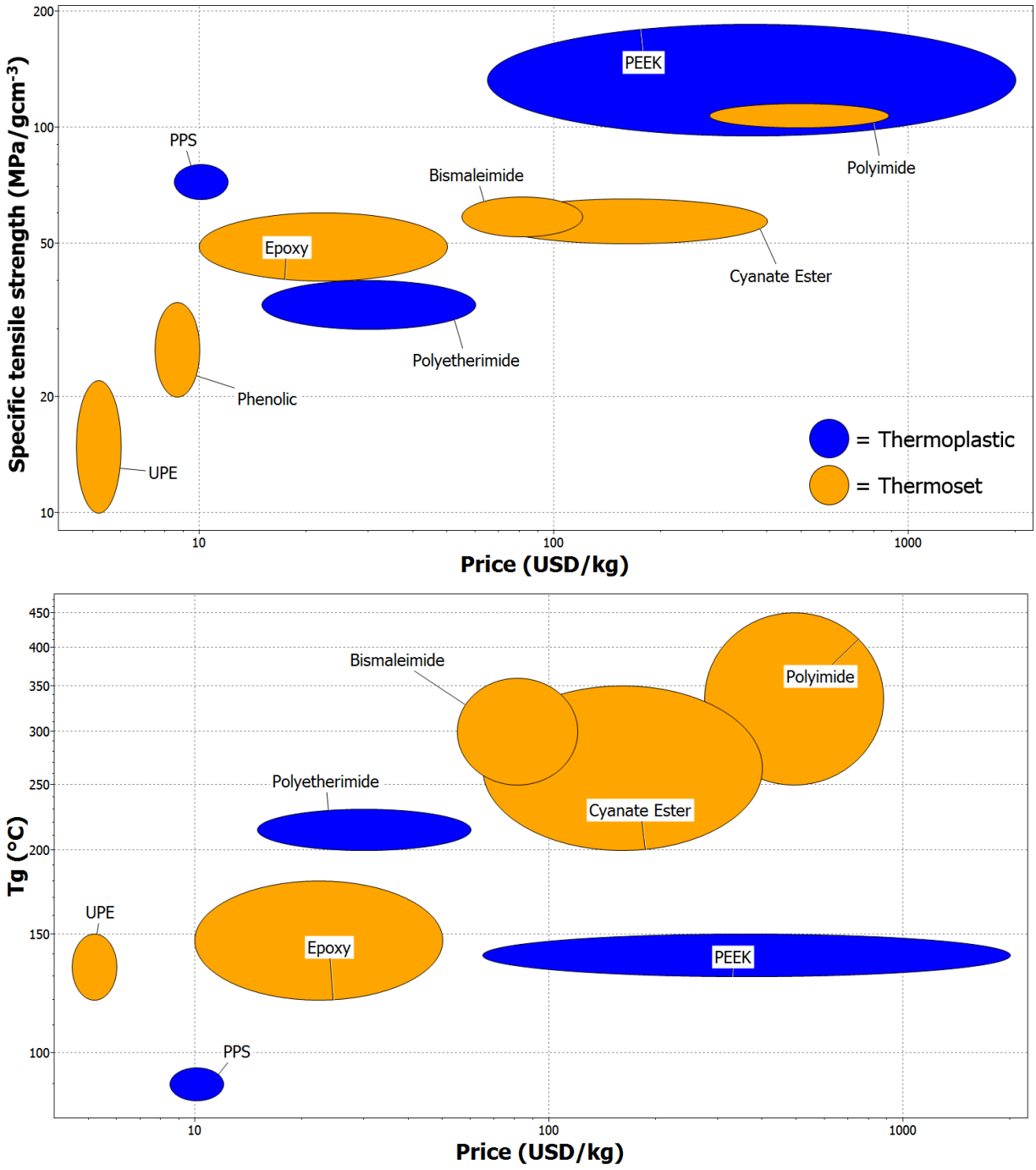


Figure 2: Comparative properties of advanced resins (redrawn from [3]**). Key: UPE = Unsaturated Polyester, PPS = poly(phenylene sulphide), PEEK = poly(ether ether ketone)**

A consideration of both performance and cost places BMIs squarely between epoxy resins and cyanate esters, potentially filling a niche that epoxies fail to occupy at a price that is competitive with lower performance (difunctional) cyanate esters (Table 2). The prices given should be treated with caution, not only because they are derived from different sources, spanning some fourteen years in a volatile market, but monomer prices are notoriously difficult to quantify. This is particularly true of niche products since they are influenced by a number of factors *e.g.* strategic

pricing, market penetration, strategic partnering, *etc.* Nevertheless, each source is self-consistent so the relationships between the different competitor resins give reasonable guidance.

Table 2. Representative prices of competitor resins

RESIN	**AUD/kg in 2006** [4]	**£/kg in 2001** [5]	**$/lb in 2015 (CF prepreg)** [6]	**€/litre in 2004** [7]	**$/lb in 2002** [8]
Epoxy	3.4	2-15	70	4-10	5
BMI	5.0	>50	75	-	-
Cyanate	-	40	-	24-60	50
Polyimides	1900	>80	-	80-260	100

1.1 Historical Perspective

The interest in BMIs, from both a scientific and technical viewpoint, surged worldwide throughout the 1980s with numerous research articles published from several well-established groups, each reporting a number of increasingly exotic 'first generation' BMIs. The synthesis of these monomeric building blocks is comparatively straightforward and several routes are available [9–11]. In the most commonly-used route, the appropriate diamine is treated with two equivalents of maleic anhydride in the presence of acetic anhydride and sodium acetate to effect dehydration and cyclisation of the resulting maleamic acid (Figure 3) [12]. DMF is used as the solvent in this reaction.

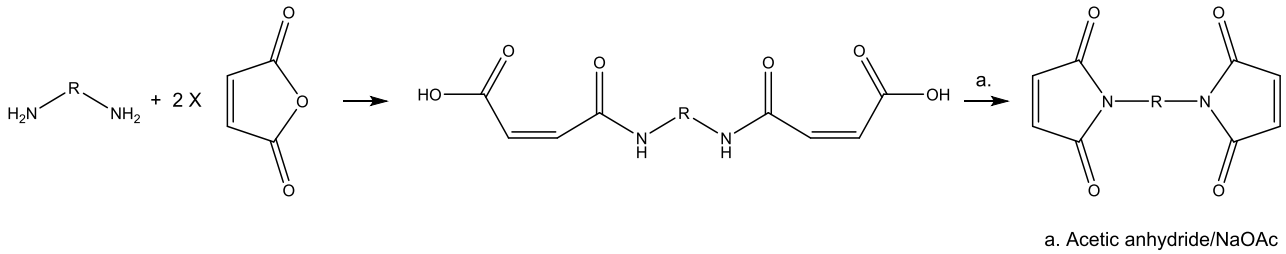


Figure 3 Typical synthetic mechanism for commercial BMIs.

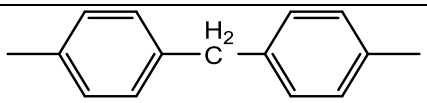
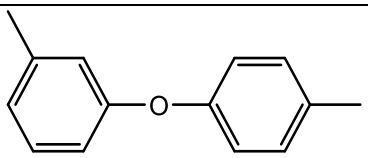
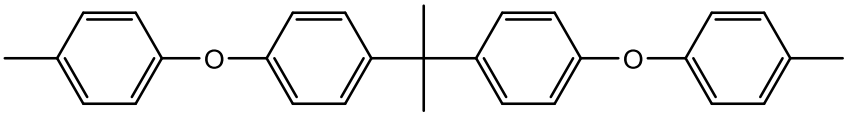
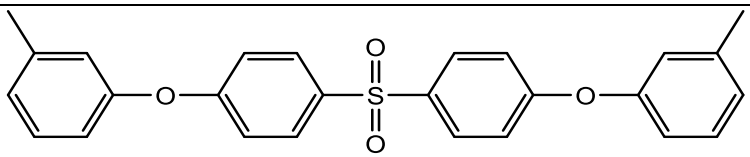
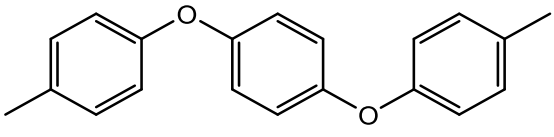
As a consequence, the backbone structure of a BMI can be readily tailored to produce materials with different properties. The versatile maleimide functional groups are able to undergo a range of useful, addition-type chemical reactions including ene-Alder, Diels-Alder, Michael addition and free-radical reactions depending on the other species present in the reaction mixture. An advantage to these reactions is that they do not produce volatiles, thus limiting void formation in the resin. The molecules are also able to undergo homopolymerisation at high temperatures (in excess of 180 °C), resulting in the production of highly crosslinked three-dimensional networks. The high degree of

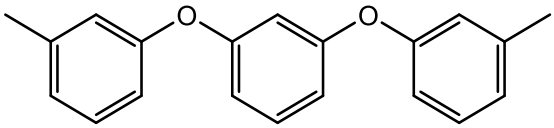
crosslinking is responsible for the excellent elevated temperature performance of these materials, however it is also the reason behind the biggest drawback associated with BMIs: the cured polymers are brittle, with low fracture toughness. While this is also the case for many other thermosets, such as multifunctional epoxies, the issue is exacerbated in BMIs by the presence of polar carbonyl groups, which leads to ordered stacking of the polymer chains and less opportunity for energy dissipation [13]. Consequently, the drive to reduce the inherent brittleness of BMIs features strongly in many published research studies.

1.2 Conventional 'first generation' BMI systems

Since the initial publications concerning thermosetting bismaleimides there have been a vast array of different monomers and reactive systems investigated. For example, in 1990, Stenzenberger listed some thirty or more experimental monomer systems with representative physical properties [14] Representative examples of the most commonly researched monomers are given in Table 3 with selected properties of interest.

Table 3 Representative experimental monomers and selected physical properties (M_p = melting point)

-R-	**M_p (°C)**	**Cure Onset (°C)**	**Cure Peak (°C)**	**Cured T_g (°C)**
	155-168	174	235	342
	212	217	236	313
	158-163	203	302	312
	104	198	211	288
	239	-	252	-

	163	-	254	-

The simplest strategy, which was pursued in many studies during the 1980s [15–17], involved increasing the distance between the maleimide rings (often in the form of 1,4-disubstituted aromatic rings bridged with ether, sulphonyl or isopropylidene moieties) in order to decrease the crosslink density with the aim of increasing rotational freedom. However, while the approach certainly yielded polymers of high thermal stability and elevated char yields compared with the lower molecular weight monomers, which contain lower proportions of aromatic carbon, it was not particularly successful in tackling brittleness, the Achilles' heel of the BMI. An extension of this method was to produce a BMI-terminated aspartimide adduct based on the rapid Michael addition reaction of a diamine with two equivalents of BMI (although the exact stoichiometry governed the length of chain between crosslinks) [18]. Although not a 'classical' linear polyaspartimide, the materials clearly have their roots in the pioneering work of Crivello during the 1970s [19]. This synthetic method was basis of early commercial BMIs such as Kerimid 601 (marketed by Rhone Poulenc) (based on bis(4-maleimidophenyl)methane, BDM, and bis(4-aminophenyl)methane) (also known as methylene dianiline or MDA) (Figure 4) [20]).

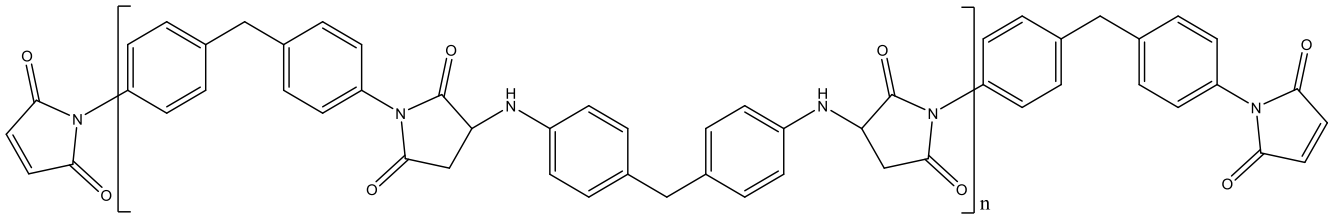


Figure 4: Structure of commercial BMI (Kerimid 601 and Compimide 200)

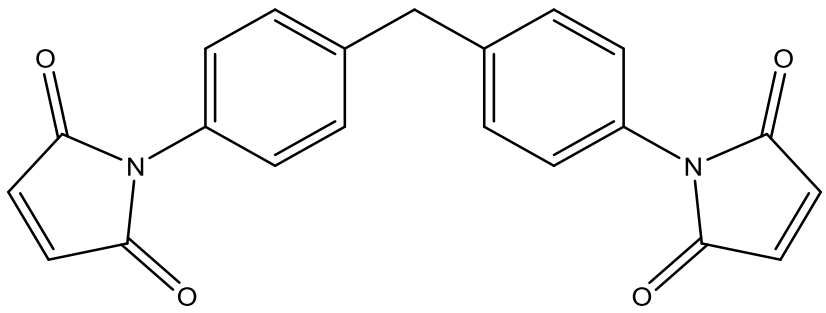
Whilst some improvements in fracture toughness were observed (increasing by over 100 %), the inclusion of succinimide rings and secondary amine moieties led to less thermally stable polymers with lower glass transition temperatures (T_g = 260 ºC would be typical for cured Kerimid 601). The residual free MDA in Kerimid 601 was around 6-12 % and was a cause of significant concern since MDA is considered a potential occupational carcinogen by the US National Institute for Occupational Safety and Health and classified by the ECHA as a 'substance of very high concern' (SVHC) and placed on the authorisation list. The Occupational Safety and Health Administration has set a permissible exposure limit at 0.01 ppm over an eight-hour time-weighted average, and a short-term exposure limit at 0.10 ppm [21], making it increasingly difficult to market MDA-based

commercial products. Nevertheless, the basic approach has stood the test of time and Compimide 200 is based on the same chemistry and structures, but is significantly more refined with a dramatically reduced MDA content (< 0.1 %).

The high melting temperature of BMI monomers, which are typically crystalline due to the strong interaction between carbonyl groups in the imide rings, provides a processing challenge. Compimide 353 was developed in order to address this [22]. The low melting, amorphous resin blend comprises bis(4-maleimidophenyl)methane (55%), 1,5-bismaleimidotoluene (30%), and 1,6-bismaleimido-2,2'-dimethyl-4-methylhexane (15%) and displays low viscosity at 110°C. The reactivity of this system was studied in detail by Pritchard and Swan [23]. Whilst the base polymer blend was not especially tough, it was formulated for combination with reactive toughening agents, *e.g.* Compimide TM123, which contain alkenyl moieties and are addressed in a subsequent section. Furthermore, this concept has been taken forward further with the incorporation of thermoplastic toughening agents [24], since the low viscosity of such systems aids their processing.

1.3 Second generation 'toughened' BMI systems

The majority of reports concerning both academic research and industrial development have centred around the combination of BDM and diallylbisphenol A (DABA), originally marketed by Ciba Geigy as Matrimid 5292 (Figure 5) [25], which can now be viewed as the benchmark BMI system against which all others are compared. This situation has arisen due to the superior toughness, temperature performance and processability compared to the aforementioned 'first generation' BMI systems, as well as the availability and comparatively low cost associated with the two monomers [22].



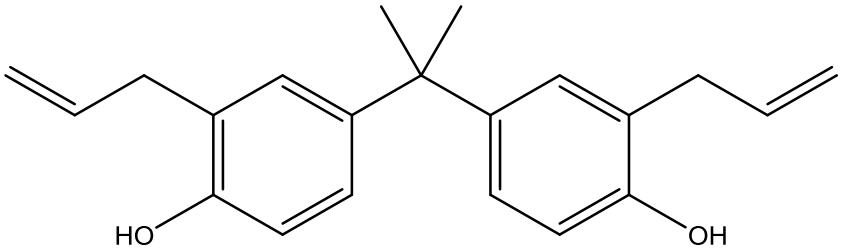


Figure 5: The structures of 4,4'-bismaleimidodiphenyl methane (top) and diallylbisphenol A (bottom), the most common constituents of BMI systems.

The reaction between BMI monomers occurs by a thermally-initiated free radical reaction between the double bonds of adjacent molecules, leading to a high degree of crosslinking. This has long been known to be the mechanism of reaction for homopolymerisation, but the situation becomes increasingly complex upon the addition of groups with different functionalities such as DABA [26]. Throughout the 1990's, a number of detailed investigations into the cure characteristics of BDM/DABA were carried out using infrared (IR) spectroscopy and differential scanning calorimetry (DSC). It has been observed that the principal reaction occurring in this blend is an alternating copolymerisation between the two different monomers (Figure 6), with homopolymerisation of the BMI units only occurring in the initial stages of the reaction at higher temperatures (*i.e.* above 200°C) [27].

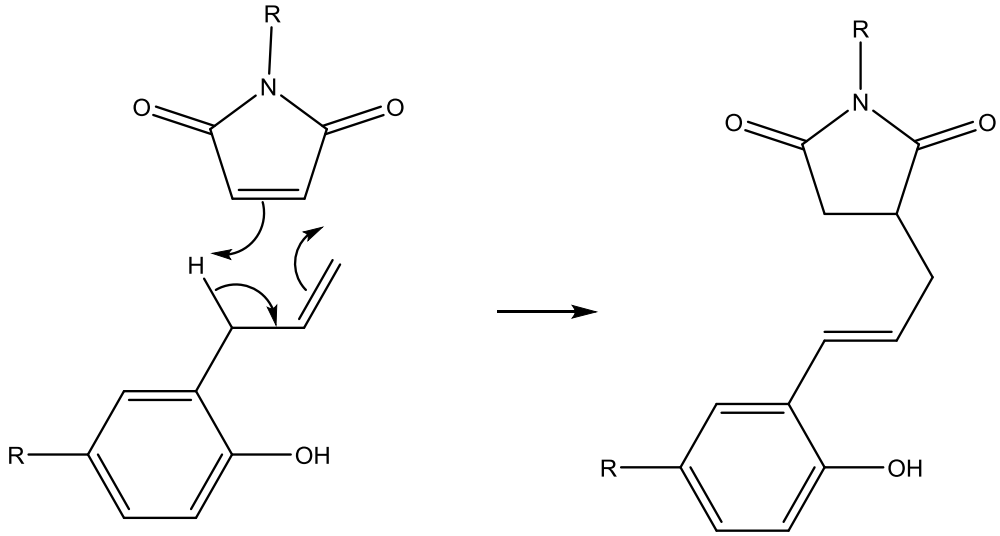


Figure 6: Hypothesised mechanism of the ene reaction that is thought to occur between allyl and maleimide groups (*N.B.*, half of each molecule shown).

This is evidenced by the occurrence of an almost 1:1 consumption ratio between characteristic IR signals for both BMI and DABA allyl groups. Crosslinking then proceeds by chain extension reactions between the newly formed 1-propen-1-yl groups and BMI monomers, in parallel with the

ene reaction [28]. It is thought that the reaction between these two groups proceeds down a pathway with a lower activation energy than BMI homopolymerisation, therefore allowing it to proceed at lower temperatures, and more rapidly. This theory is further backed up by both fluorescence and UV spectroscopic techniques, which show an initial increase in propenyl signals that then decrease as the reaction proceeds [29].

It was initially thought [30] that the 'ene' reaction was followed by a Diels-Alder reaction between the newly formed di-ene and a maleimide group, a strong dienophile (Figure 7). However, based on the rates of consumption of the different functional groups it has been shown that this does not occur in the polymerising system, probably due to steric hindrance [28]. Comparing results with a model system using monofunctional monomers, where the Diels-Alder reaction has been shown to take place, confirms this theory.

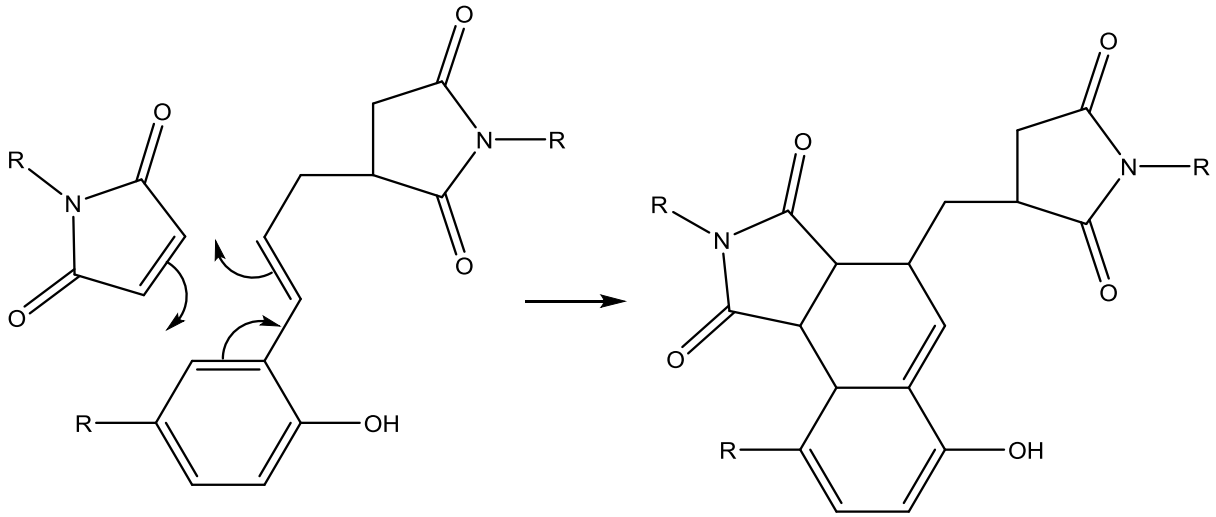


Figure 7: Hypothesised mechanism of the Diels-Alder reaction originally thought to succeed the ene reaction (*N.B.*, half of each molecule shown).

Another reaction that occurs during cure is the condensation of the DABA hydroxyl groups to form ether linkages. Interestingly, this reaction only occurs in the presence of the BMI comonomer; when DABA is homopolymerised there is no evidence of dehydration up to 250°C. This can be potentially problematic for two reasons. Firstly, this reaction leads to the evolution of water, increasing the risk of bubbles or voids forming in the cured material, which is particular problem in a reinforced composite. Secondly, the conversion of this reaction during standard cure cycles is often low (~50%) [31]. If the cured material is then used extensively at elevated temperatures, further curing can slowly take place and decrease the toughness of an already brittle system.

While this system is now very well characterised, there is a raft of new and modified systems available. A similar 'reactive diluent' concept has also been applied to propenyl-substituted

comonomers, which are able to react with bismaleimides *via* Diels-Alder addition [32]. A commonly used example of such a molecule is 4,4'-bis(2-(1-propenyl)phenoxy)-benzophenone (marketed by Evonik as Compimide TM123, Figure 8), which imparts improved processability and toughness at the cost of a decrease in T_g.

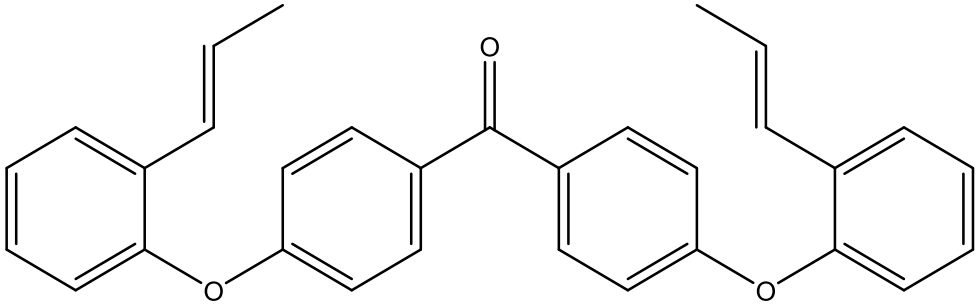


Figure 8: Structure of reactive modifier Compimide TM123.

The alkenyl-based chemistry (involving ene-Alder or Diels-Alder reactions) still forms the basis for the most successful and best-established commercial toughened BMI systems. While the hypothesised nature of the co-reaction mechanism has altered over time with the release of more research studies, the resulting copolymers are undoubtedly the bench mark BMI against which modern BMIs must be measured. `

1.4 Background to the present review

The outpouring of work during the 1980s encompassed an extremely dynamic period of synthetic chemistry and culminated in a series of excellent reviews by Stenzenberger [14,33], who concisely summarised the early progress in the area. These reviews outlined a number of fundamental aspects on which future chemists and technologists would need to focus if BMIs were to develop and become a commercially acceptable standard. These aspects were mainly based around the synthesis of new monomers, blends and systems in order to improve upon the biggest drawback of BMIs, namely their poor toughness, without sacrificing their advantageous properties and processing characteristics. It is the authors' intention to evaluate the development of BMI chemistry during the intervening twenty-six years according to the predictions of Stenzenberger, which are outlined in this review. These research routes can be broken down into three main categories: synthesis of novel bismaleimide building blocks; incorporation of new thermoplastics to improve toughness; blends with new thermosetting comonomers and each will be addressed below. Additionally, the more recent fields of nanocomposites and smart materials are discussed, along with research on BMI matrix composites.

2. DEVELOPMENT OF NOVEL BMI MONOMERS

Perhaps the most obvious method for introducing new or refined properties into conventional BMI systems is to alter the monomer's chemical structure. In theory, the backbone structure between the two reactive maleimide groups can be readily altered either by modification of existing diamines or by using different starting materials to yield exotic structures. There are numerous examples in the literature of new monomers being synthesised in order to try and improve on a particular performance aspect of BMIs, which are outlined in this section of the review.

2.1 Improving toughness in cured BMIs

The drive to produce resins with superior toughness has led to numerous attempts to alter monomer structure to reduce the brittleness of the materials. This can be achieved by two means. Firstly, as has been described previously, the crosslink density of the cured material can be decreased by increasing the molecular weight of the monomer, or the distance between the two functional end groups using chain extenders such as diamines [34]. The second option is to introduce more flexible linkages into the network structure, usually undertaken by incorporating ether groups into the monomer backbone (Figure 9) [16,35]. As expected these modifications lead to an increase in the energy absorbing ability of the materials due to a greater degree of molecular freedom, thus resulting in improved impact performance. However, this increased flexibility inherently leads to a lowering of the glass transition temperature of the polymer and a reduction in modulus. This means that the benefit of using BMIs is impacted, bringing the performance of the material closer to the cheaper, industry standard epoxies.

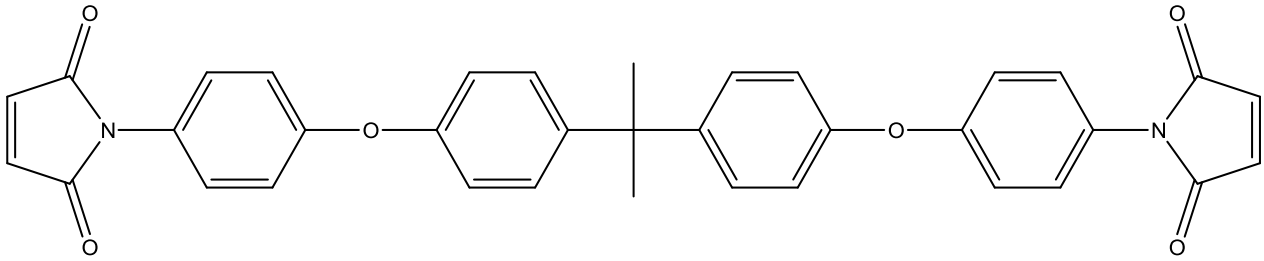


Figure 9: Structure of 2,2'-bis[4-(4-maleimidophen-oxy)phenyl)]propane (BMPP)

This strategy has proved to be successful to the point that 2,2'-bis[4-(4-maleimidophen-oxy)phenyl)]propane (BMPP) is now a commercially available monomer containing ether groups. Mixing this monomer into the conventional BDM/DABA system leads to the formation of a material with promising properties [36]. Firstly, rheological characterisation showed that the uncured blend is able to maintain a low viscosity over a wide temperature range (100 – 180 °C), meaning that the material has a broad processing window but with no change in curing temperature. Moreover, the impact strength and fracture toughness (both K_{IC}, the critical stress intensity factor,

and G_{IC}, the critical strain energy release rate) are increased whilst a glass transition temperature (T_g) of 298 °C is maintained in the best performing variant.

In 2001, an attempt was made to improve upon the successful BDM/DABA resin system by incorporating the features of both components into a single monomer (3-(allyloxy)-2-hydroxypropyl 4-maleimidobenzoate Figure 10) and thus simplify the system [37]. This was achieved by using epoxy chemistry to produce a building block containing a maleimide group, an allyl group and ether linkages. However, the material proved ineffective due to a lack of processability and poor moisture resistance characteristics, as might be expected due to the presence of a hydrolysable ester group and multiple heteroatoms.

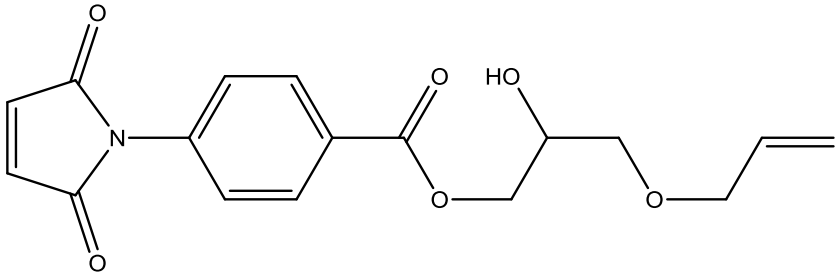


Figure 10: Structure of 3-(allyloxy)-2-hydroxypropyl 4-maleimidobenzoate.

2.2 Improving processability of BMI monomers

Evsyukov *et al*. were interested in producing materials with improved processability while reducing the reliance on monomers that are either toxic themselves or are fabricated from toxic precursor diamines [38]. They converted *m*-xylylenediamine into a BMI monomer (Figure 11) using the conventional 'maleic anhydride' synthetic method (Figure 3). This diamine is attractive due to its short, aromatic backbone, ready availability (thanks to its application as an epoxy curing agent) and the fact that it is comparatively non-toxic. It was found that the cured BMI based on this molecule possessed similar mechanical properties to 4,4′-bismaleimidodiphenylmethane but with significantly lower viscosities enabling easier processing. The drawback to the new monomer is that it led to a lowering of the final T_g of the polymer network, however it was still greater than 270 °C.

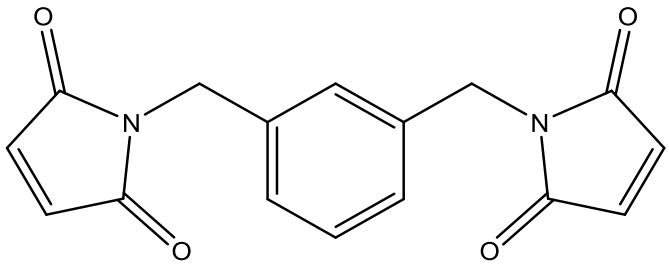


Figure 11: The structure of xylylenediamine based BMI.

Another route for improving the processability is to introduce bulky, soluble side groups into the monomer backbone to enable dissolution in industrially acceptable solvents and to lower the material's melting point. It is important that such modifications to the monomer do not impact on the thermal or mechanical performance of the system and, consequently, highly aromatic side groups *e.g.* fluorenyl cardo groups (Figure 12) [39,40] tend to be of interest.

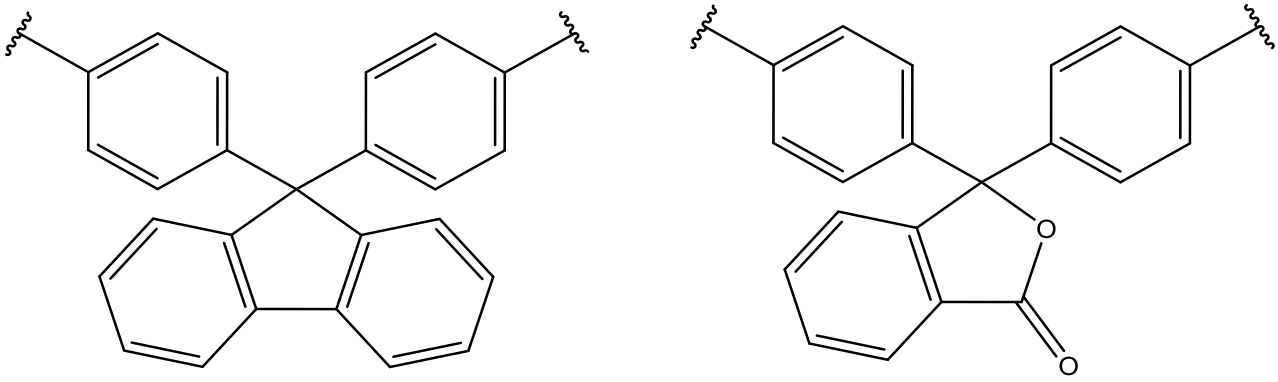


Figure 12: Fluorenyl cardo (left) and phthalide (right) groups that have been incorporated into novel BMI monomers.

A BMI monomer containing both fluorenyl cardo and aryl ether linkages was found to be soluble in a range of solvents including acetone, toluene and dichloromethane (DCM). Additionally, the thermal decomposition temperature of the cured material was over 400 °C, however no information was given with regards to the T_g or mechanical properties of the cured resin [41]. A similar solubility was observed for a range of BMI monomers containing the phthalide moiety, but it was found to have a high melt viscosity and cure temperature, therefore adversely affecting processability. A further study blended one of these monomers (dubbed PPBMI) with BDM/DABA [42]. When the PPBMI/MDM/DABA ratio was 3:7:2.61, a resin with excellent properties was obtained. This material could be cured with a conventional cure cycle, had a dry T_g of 292 °C, and outperformed the standard MDM/DABA mixture in terms of impact strength, water absorption and flexural modulus. Tertiary butyl substituents have also been used to widen the processing window [43]. Adding a ^{t}Bu group to the phenyl ring of a BMI monomer backbone led to the lowering of the melting point by 120 °C, and at the same time lengthening the processing window from 1 °C to 71 °C. There was, however, a 30 °C reduction in the softening temperature of the resin.

More recent work has begun to look at the synthesis of asymmetric monomers as a way to reduce the melting points of uncured BMI systems, however this work is still in its infancy [44].

2.3 Improving high temperature performance of cured BMIs

The vast majority of BMI monomers contain aromatic groups in order to impart thermal stability and stiffness to the three-dimensional network. Wang *et al*. suggested that these properties might be improved, along with moisture absorption and chemical resistance characteristics, by incorporating naphthalene groups into BMI monomers as either 'in chain' as part of the backbone, or as a pendant group (Figure 13) [45,46]. In the case of the 'in chain' monomer, it was found that the T_g of the material was improved compared to a phenyl-substituted analogue, and the processing window was widened thanks to lower melting temperatures. Monomers with a naphthalene side group produced polymers with high T_g and thermal stability. The toughness of these polymers is not mentioned in either instance, although it might be expected that these modifications to the monomer may lead to decreases in the impact resistance due to the rigidity of the naphthalene group.

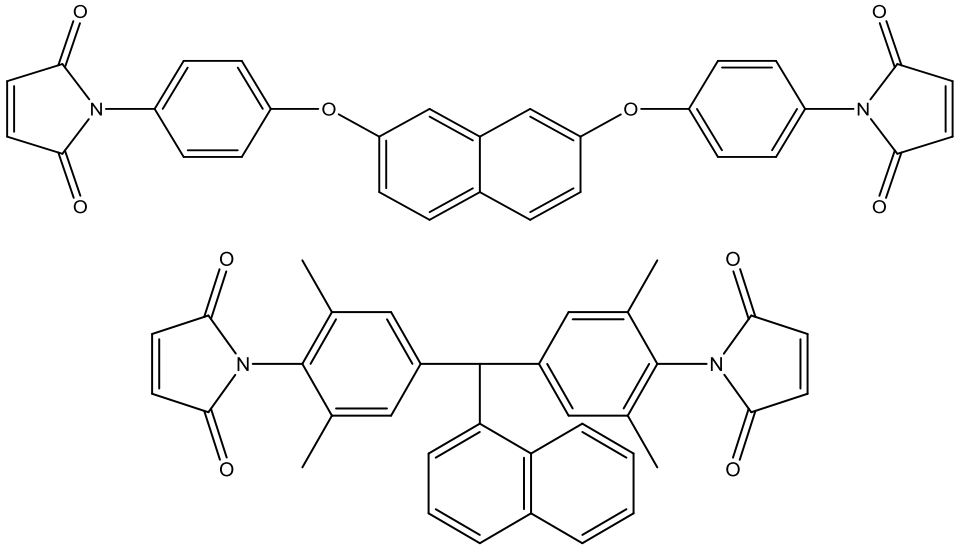


Figure 13: Examples of BMI monomers that feature naphthalene moieties in their structure.

Similarly, there are several examples of monomers that have been produced containing 1,3,4-oxadiazole moieties (Figure 14) to produce similar performance improvements [47]. The synthesis of monomers containing this thermally and chemically stable group, which has also been examined in epoxy chemistry [48], enabled the production of processable polymers with no observable T_g up to 400 °C and an onset of thermal degradation over 490 °C. Again, the toughness of this system was not reported.

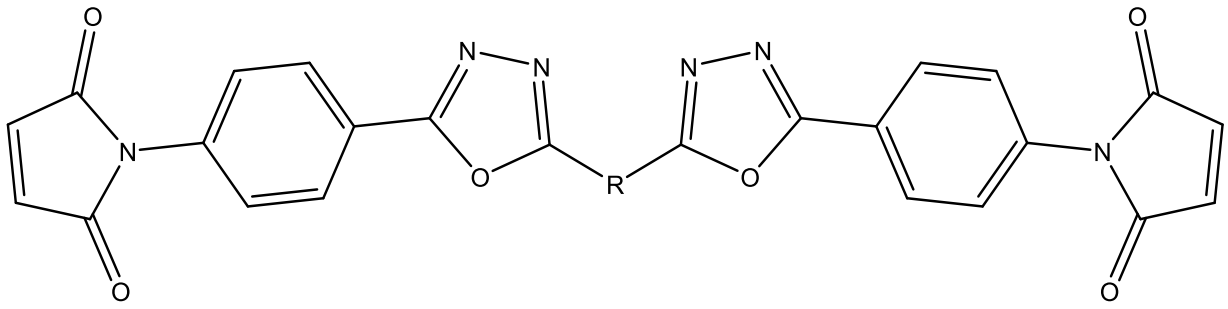


Figure 14: Oxadiazole containing BMI monomer.

There is generally less overt pressure to improve the thermal resistance of BMIs since the initial degradation temperatures and char yields are high, however it is axiomatic that for the development to find commercial acceptance, improvements in thermal stability must be matched by commensurate increases in fracture toughness without compromising processability.

2.4 Improving flame resistance in cured BMIs

During the 1980s, a number of studies by IK Varma *et al.* explored organophosphorous BMIs, generally based on lower molecular weight, bisphenyl based, BMIs [49]. Among other groups, these incorporated phosphoryl ester moieties. Since the turn of the 21st century, the legislative environment has changed significantly with bans placed on many halogenated flame retardants (FRs) by both the USA and the EU leading to a much greater interest in phosphorus based additives [50]. In a recent study, researchers incorporated a more widely used phosphorus based, flame retardant, aromatic moiety (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, DOPO) into a BMI monomer (Figure 15) [51]. It was hoped that this would improve the materials flame resistance and increase the solubility of the monomer in low-boiling (and less harmful) solvents, all while maintaining the desired thermal, electrical and mechanical performance. Again, the monomer was prepared by imidising an appropriate diamine using maleic anhydride and the conventional route. It was found that the new monomer was readily soluble in a range of common organic solvents including acetone and 1,4-dioxane, enabling it to be processed without the need for the traditional harmful solvents. Interestingly, the DOPO-BMI molecule did not exhibit a melting point, instead going through a glass transition at around 135 °C. This suggests that the material forms an amorphous glass rather than a crystalline solid as is the case with the majority of traditional bismaleimide monomers. The new monomer improved the char yield in air when incorporated into a thermoset from 1.8 to 50 % at 700 °C, whilst maintaining a high T_g of over 300 °C.

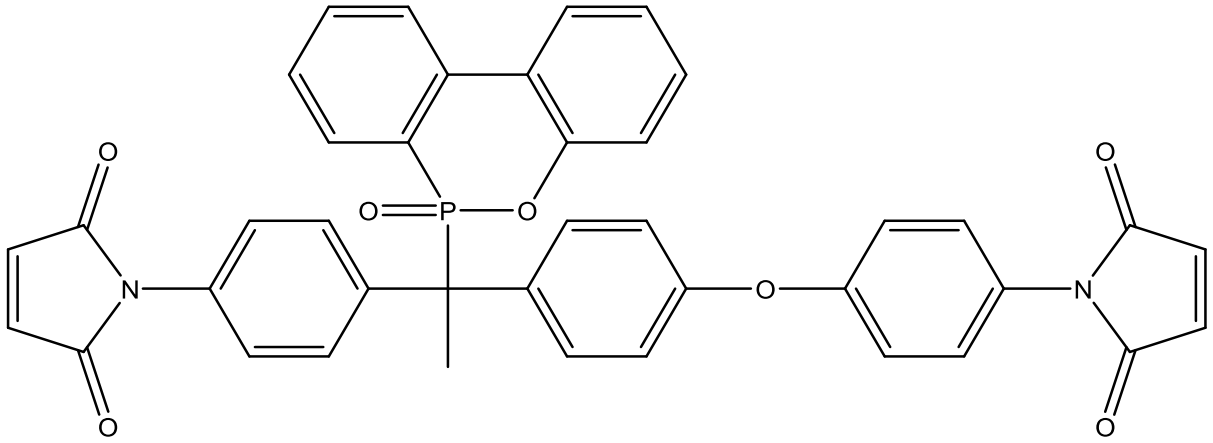


Figure 15: The chemical structure of a DOPO containing BMI monomer designed to impart improved flame retardency to the resin.

Similar investigations have been undertaken where the DOPO molecule is added as a separate resin component, rather than as part of the monomer structure [52]. This approach reduces the complexity of the synthesis of the reactants. DOPO is able to bond covalently to BMI groups *via* a Michael addition reaction, however this results in a decrease in the materials crosslink density and hence its T_g. The positive aspect of this system is that the heat release rate and char yield are greatly decreased and increased, respectively, compared to the unmodified BMI. This improvement coincides with a significant reduction in dielectric constant and loss (from 3.25 to < 3.00 and 0.01 to 0.003, respectively, at 10^7 Hz), which is particularly useful for electronic applications. It was also found that when this DOPO-modified BMI resin was used in a composite, there was improved adhesion at the fibre resin interface leading to improved mechanical properties such as interlaminar shear strength (ILSS), which increased from 11 to 22 GPa [53]. Li *et al*. produced an alternative phosphorus-based, flame retardant monomer designed for use in BMIs that contained allyl groups (Figure 16) capable of reacting in the same way as DABA [54]. They observed that this monomer increased the char yield at 800 °C (from 23.5 to 36.5 %) and limiting oxygen index (LOI, from 26.3 to 34.7) of the BDM/DABA system, but also led to reductions in impact and flexural strength of 20.4 % and 13.6 % respectively.

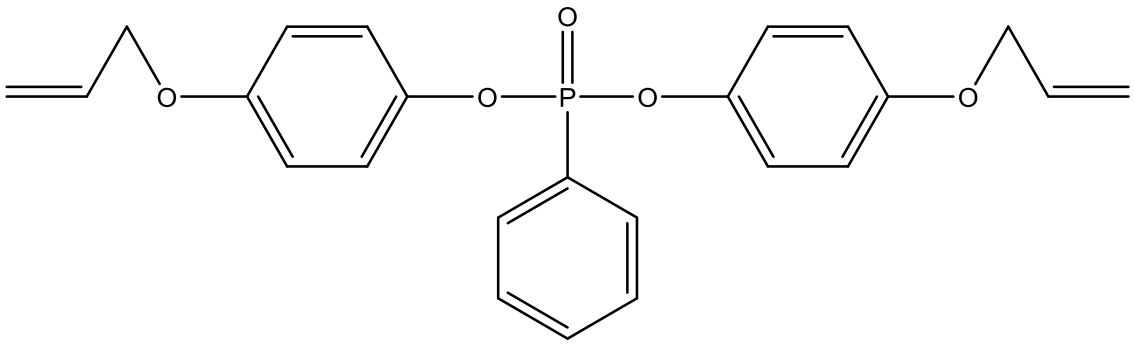


Figure 16: The chemical structure of a phosphoryl ester containing monomer designed to impart improved flame retardancy.

This is an area that will only increase in importance in the years to come. The proposed use for BMIs and their blends in thermally critical areas, particularly within enclosed interiors, means that the use of non-halogenated FRs will be employed to improve FST (flame, smoke and toxicity) behaviour.

2.5 Low modulus BMIs

While the majority of BMI systems are targeted at applications in which strong mechanical properties, such as high modulus, are required, there is also requirement for lower modulus materials. This is especially true in some electronic packaging applications, where the shrinkage of stiff BMIs after cure can lead to warping of substrates and hence part failure. One solution to this issue is the replacement of the highly aromatic backbones in conventional BMIs with aliphatic structures [55]. An example of such a structure is the incorporation of the 'C_{36}' group shown in Figure 17. By combining this group with aromatic imide extenders, a BMI monomer with thermal stability (thermal decomposition temperature (T_d) >400 °C), low modulus (<500 MPa) and low cure shrinkage is produced. This structure also imparts the added benefit of reducing the moisture uptake of the cured resin. Molecules such as this are now being incorporated into commercial systems by Hitachi Chemical Company Ltd.

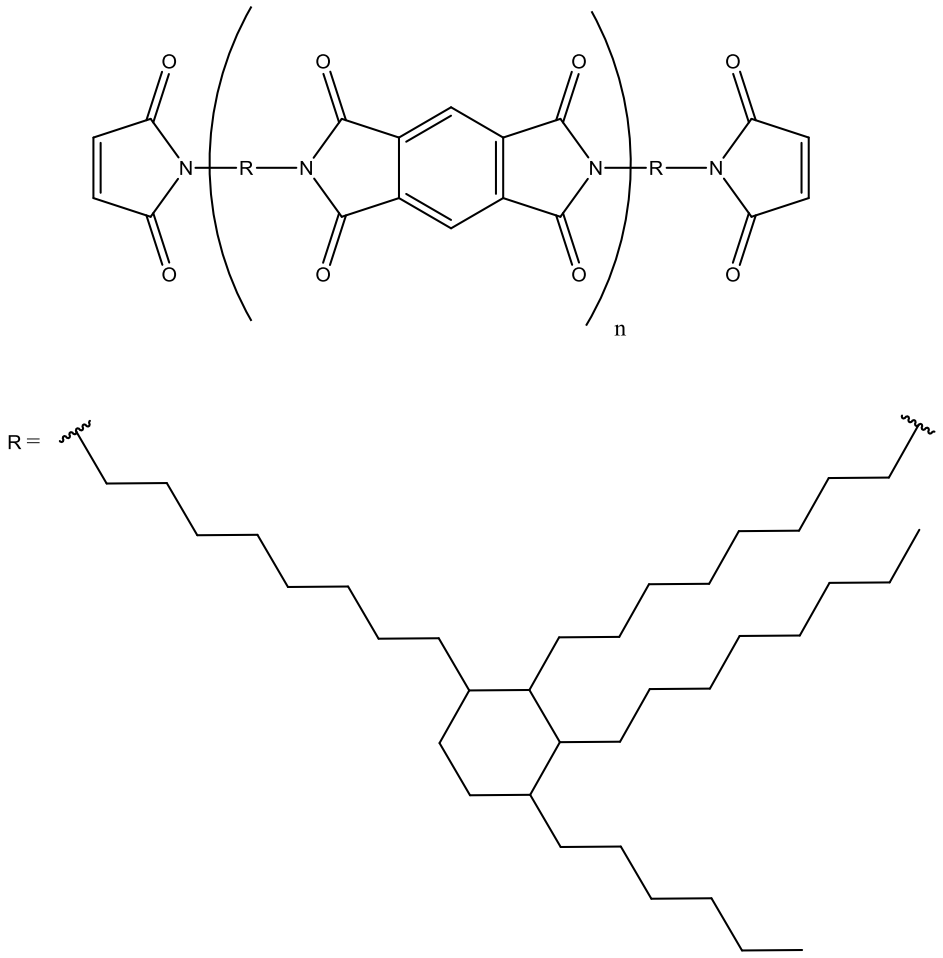


Figure 17: The structure of a C_{36} containing BMI monomer (n≈3)

This is a very exciting development as it offers the opportunity to introduce reactive toughening agents, albeit with a T_g penalty, without apparently compromising the thermal stability behaviour of the cured BMI blend.

2.6 DABA alternatives and additives

Iijima *et al.* investigated using dimethylated DABA (mDABA) (Figure 18, left) as well as a triallyl isocyanurate (TmAIC) molecule (Figure 18, middle) as potential alternatives or supplements that might alter the properties and performance of the conventional BDM/DABA system [56]. The inclusion of mDABA led to increases in fracture toughness (from 0.62 to 1.02 MPa $m^{1/2}$) and flexural modulus (from 4.02 to 4.29 GPa), however there was a large negative impact on the T_g of the resin (a drop of 118 K was observed). The use of TmAIC led to a system that exhibited retention of T_g and flexural properties alongside a modest 15 % increase in K_{IC} (achieving 0.71 MPa $m^{1/2}$). It was reported that control over resin properties was readily achieved using different reagent stoichiometries. Aijuan *et al*. added allyl methyl phenol (Figure 18, right) as an additional allyl component in order to further reduce the viscosity of the resin to render it suitable for processing

via resin transfer moulding (RTM) [57]. It was found that the viscosity of the system was sufficiently low to enable injection whilst maintaining a long pot life (≥12 hrs at 75 °C) as well as fast gel times (50 s at 200 °C). This was all achieved alongside a cured T_g of 266 °C.

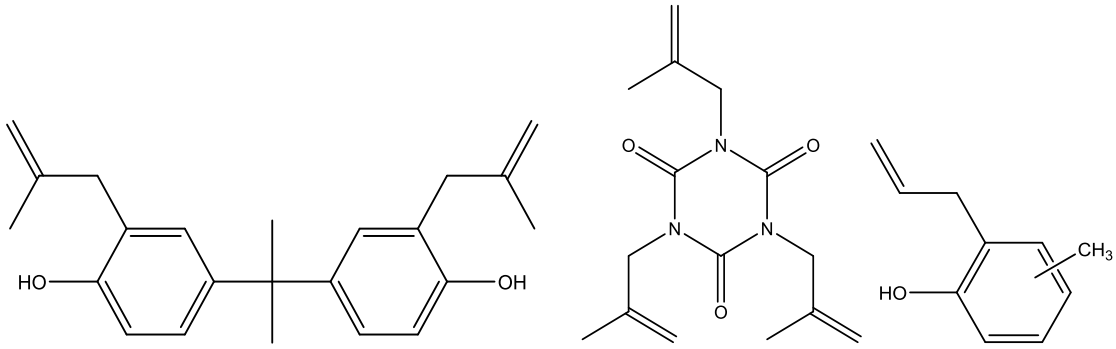


Figure 18: Chemical structures of potential DABA alternatives: mDABA (left) and TmAIC (middle), and additive allylmethylphenol (right).

Other DABA alternatives have been developed with the aim of improving multiple properties simultaneously. One example of this is the work undertaken by Sunitha *et al*. who used tris(2-allylphenoxy)triphenoxycyclotriphosphazene to enhance the flame retardancy at the same time as improving the processability and toughness of the system [58]. The materials produced exhibited improved char yield and thermal erosion whilst achieving a T_g between 240-250 °C [59].

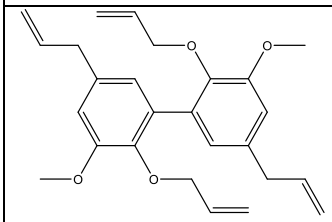
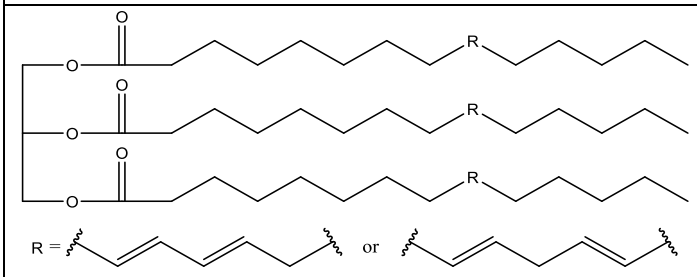
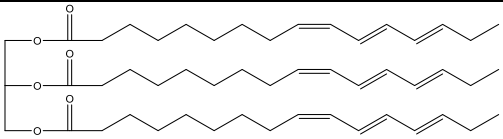
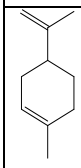
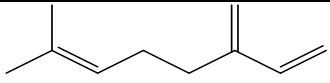
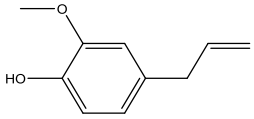
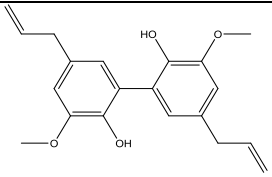
More recently, Wang *et al*. produced a series of carbonyl containing di- and tri- functional allyl containing monomers and used them as BDM modifiers [60]. These blends cured at lower temperatures than the BDM/DABA system and exhibited higher char yields at 800 °C, with yields as high as 58 wt% compared to 27 wt% for the reference system. There was also an improvement in dielectric constant at 10 GHz, from 3.10 to 2.86. This strategy for producing new BMI systems has also caught the eye commercially, with Designer Molecules Inc. having recently taken out a patent covering a large number of di-allyl compounds to be used as BMI co-monomers [61].

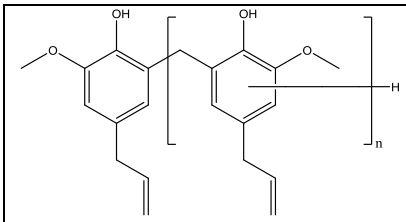
2.7 BMI co-monomers derived from naturally occurring feedstocks

In the drive for more ecologically sustainable methods of producing composite materials, interest has turned to biological or naturally occurring systems as matrix precursors [62]. This has led to the incorporation of these types of molecules into BMI systems. Shibata and co-workers have been at the head of this field, combining various, organically-derived modifiers containing unsaturated C=C bonds with BDM to produce high performance thermosets. These bio-based molecules have been produced from a range of different vegetable and plant oils [63–71]. The best performing materials in each of these studies, in terms of temperature, are summarised in Table 4. As expected, the molecules containing long aliphatic chains caused a large reduction in T_g and as such their use is not as appealing as the small molecule eugenol and terpine variants, which all show promising

temperature performance. A significant amount of work remains to be undertaken in the area, as important properties such impact resistance and water absorption have yet to be reported. Furthermore, these blends require harsh mixing and curing conditions compared to industrial standards in terms of temperature, so the processability needs to be considered as these materials are taken forward.

Table 4. Representative bio-based BMIs with selected properties when blended with BDM

Modifier	**Ratio of monomer to BDM**	**T_g (°C)**	**$T_{5\%}$ (°C)**
	1/3	>400	481
	1/2	141	441
	1/4	150	468
	1/1	365	479 ($T_{10\%}$)
	2/5	340	450 ($T_{10\%}$)
	1/3	377	478
	1/3	336	431

	1/3	365	447

Key: T_g = dry glass transition temperature of cured resin, $T_{5\%}$ = temperature at which 5 % mass loss recorded, $T_{10\%}$ = temperature at which 10 % mass loss recorded.

3. THERMOPLASTIC MODIFIED BMIs

The incorporation of thermoplastics into thermoset systems is a recognised method for reducing their inherently brittle nature and therefore improving their fracture toughness [72,73]. Unlike thermosets, thermoplastics do not contain crosslinks between adjacent polymer chains, meaning that plastic flow and energy dissipation are characteristic yielding mechanisms. The challenge in this area is to achieve the thermoplastic modification while having minimal impact on the thermal performance and processing of the system. To this end, thermoplastics with inherently good thermal properties are often selected as candidate modifiers; example polymers that have been tested in BMI systems include polyetherimides [74], poly(ether ketone)s [75] and poly(ether sulfone)s [76]. Thermoplastic toughening has been proven to be successful to the point that it has been taken up in commercially available BMI systems, as evidenced by patents published by both of the current leading composites suppliers, Hexcel [77] and Cytec [78].

3.1 Modifier variables

There are a number of polymer variables that can be altered in order to optimise the overall properties of the system and produce the most effective balance depending on application requirements. Factors that can be changed include thermoplastic loading, backbone structure, molecular weight, molecular weight distribution and end group functionality. The influence of some of these upon resin toughness was investigated by Wilkinson *et al.* in 1994 [79]. One important outcome of this work was the observation that the identity of the thermoplastic end group is important in promoting toughness. Fracture toughness values were significantly higher (by more than 50%, attaining a K_{IC} value of 1.4 MPa $m^{1/2}$) when the end groups were reactive functionalities, capable of forming covalent bonds with the BMI network during crosslinking. This is thought to be because of increased interaction between the two components and therefore reduced phase separation. It was also shown that increasing either the molecular weight or percentage loading of the thermoplastic filler will lead to an increase in fracture toughness. As these variables are increased, the morphology of the system changes from a dispersed to co-continuous followed by phase inverted, which is thought to be the most effective in terms of thermoset toughening [80].

However, as these two variables are increased, the processability and thermal performance becomes more adversely affected. As such, only moderate loadings (< 20 wt%) and molecular weights (< 15,000 g mol^{-1}) are recommended when utilising this toughening route.

3.2 Functionalised backbones

Several attempts have been made to design thermoplastics with reactive functionalities statistically distributed along the polymer chain in order to increase the adhesion of the additive with the base BMI resin. Examples include poly(arylene-ether ketone)s and poly(arylene-ether sulfone)s modified with propenyl containing reagents (Figure 19), which were both successfully synthesised at intermediate molecular weights (≈50,000 g mol^{-1}) [81,82]. In both instances, it was observed through scanning electron microscopy (SEM) and DSC that there was good adhesion between the two phases indicating successful chemical reaction between the two. However, it was found that as the concentration of propenyl groups on the backbone was increased, the toughening ability of the thermoplastic was decreased to the point that there was no benefit compared to the neat resin. This is likely to be because the increasing functionalisation leads to an increase in crosslink density (with co-reaction of propenyl on adjacent chains competing with propenyl-BMI co-reaction), ultimately tending towards a situation where the thermoplastic is acting in the same way as a low molecular weight co-monomer. As such, this method has not gained much traction in terms of being taken forward for further research and application.

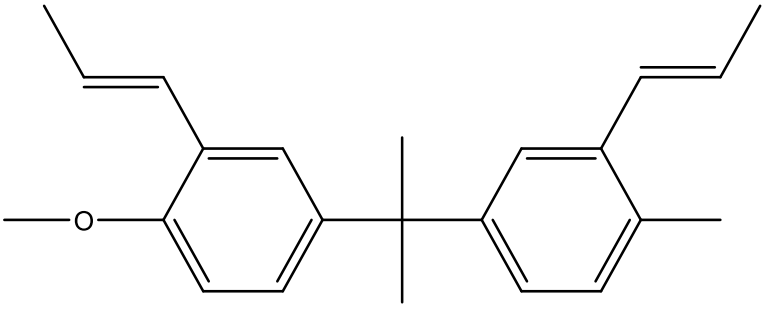


Figure 19: Propenyl containing building block that can be incorporated into poly(aryl ether) and its derivatives.

Similarly, allyl groups have been used to functionalise modifier backbones. An example of this is the work by Satheesh *et al.* who adapted an aralkyl phenolic resin, typically used as high performance thermoset, by converting the hydroxyl groups into allyl ethers [83]. Incorporating this phenolic into a bismaleimide system led to a material with tuneable properties: increasing the amount of BMI component improved its thermal performance (T_g up to 280 °C) whilst increasing the phenolic percentage improved its toughness (impact strength maximum of 217 kJ m^{-2}) .

3.3 Low molecular weight thermoplastics

One of the primary issues with using thermoplastics as toughening agents in advanced thermosets is that they inherently raise the viscosity of the uncured resin. As the molecular weight of the thermoplastic becomes greater, the viscosity increases exponentially ultimately leading to the systems becoming unprocessable. This led to researchers investigating the toughening ability of very low molecular weight (M_n < 5000 g mol^{-1}) high performance thermoplastics [84]. They found that the use of a low molecular weight polyimide in BDM/DABA yielded an autoclave processable system with significant increases in fracture toughness (75% improvement, to attain a K_{IC} of 0.7 MPa $m^{1/2}$) without adversely affecting the material's T_g. Whilst the viscosity of the resin was increased by an order of magnitude (from 0.6 to 16 Pa S) compared to the neat blend, this increase is far lower than that witnessed for higher molecular weights and the handling of the material is facile. An alternative approach that has been mooted is the use of comb-shaped thermoplastics (*i.e.* containing long pendants) rather than traditional linear variants [85]. The reasoning behind this idea is that the thermoplastic molecular weight could be increased without the concomitant rise in viscosity. It was found that a reactively functionalised comb-shaped imide oligomer could increase the toughness of the BMI system by 150% to 1.05 MPa $m^{1/2}$, again while the system maintained adequate processability and temperature performance.

3.4 Hyperbranched polymers

Hyperbranched polymers are interesting potential toughening agents for thermosets because of their low viscosities, therefore giving the possibility of increasing processability and toughness concurrently. The first example of the application of this ideas to BMIs was in 1999, when Gopala *et al*. used a hydroxyl-terminated hyperbranched polyester to modify a BDM/DABA system [86]. They were able to produce large increases in toughness (138 %) over the neat resin (*i.e.* from 0.42 to 1.0 MPa $m^{1/2}$), but there were also large losses in terms of T_g (decreasing from 265 to 225 °C) and modulus (decreasing from 3 to 0.7 GPa). It was also found that while the processability was improved by lowering blend viscosity, the effect was no better than that obtained from an easier to synthesise linear analogue of the hyperbranched polymer.

Qin *et al*. synthesised an allyl terminated hyperbranched poly(ether-ketone-imide) (Figure 20) as a BMI modifier to try and overcome the shortcomings associated with the aliphatic polyesters used previously [87,88]. Unusually for a toughening additive, this approach led to improvements in all of the key areas of processability, T_g (from 244 to 264 °C), modulus (from 3.4 to 3.8 GPa) and fracture toughness (from 0.48 to 0.55 MPa $m^{1/2}$). While this is highly beneficial, it must be noted that there was only a small increase in toughness, especially when compared to the aforementioned hyperbranched polyester. The authors suggested that the degree of polyimide branching or the

branch end-cappers could be modified to increase the toughness further, but there has been no mention of this in the literature since.

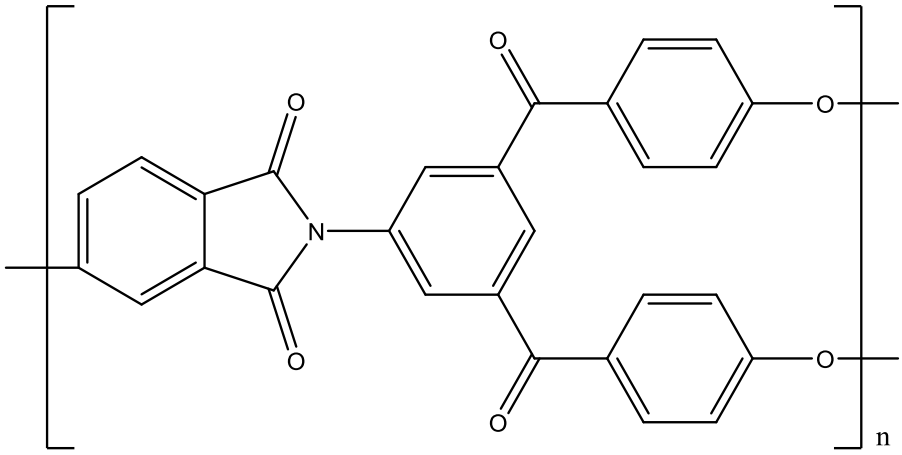


Figure 20: Chemical structure of the hyperbranched poly(ether-ketone-imide) modifier.

Polysiloxanes are another example of hyperbranched polymers being added to BMI systems in order to enhance their properties. It has been found that these additives can lead to increases in the flame retardancy and toughness of the thermoset (*e.g.* an addition of 15 wt% leads to an increase in impact strength from 10.5 to 19 kJ/m^2 and char yield at 800 °C from 27.8 to 53.7 wt%) without impacting the stiffness and T_g too severely [89].

3.5 Reactive elastomers

Elastomers are another family of polymers that have been used as toughening agents in BMI systems. Elastomers are typically characterised by high failure strains and toughness, making them attractive as resin modifiers. In 1997, the liquid elastomer carboxyl-terminated acrylonitrile butadiene (CTBN, Figure 21) was used to increase the flexibility of Compimide 353. At 30 °C, the addition of 40 wt % of this polymer increased its lap shear strength from 14.7 to 46.1 MPa. However, this performance was not maintained at 200 °C, where the incorporation of the elastomer led to reduced strength. This shows that the elastomer had a large, negative impact on the thermal properties of the material.

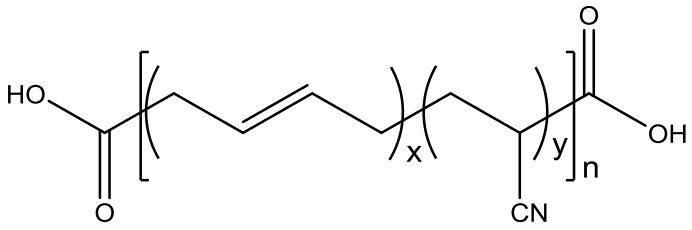


Figure 21: The structure of a CTBN elastomer used to modify BMI.

A patent from 1996 details the use of low T_g (<10 °C) acrylonitrile/butadiene elastomer particles as toughening agents in BDM/DABA [90]. It is claimed that the use of 5 wt% of the elastomer leads to a 51% increase in compression after impact (CAI) strength from 156 to 236 MPa. However, no mention was made of the impacts on other properties; thermal properties of the material are almost certain to have been reduced.

3.6 Particle toughening

While the thermoplastic modifications of BMIs presented thus far are focussed around the blending or solvation of the thermoplastic in the thermoset resin, it is also possible to increase resin toughness using preformed thermoplastic particles. Wei and Sue used preformed polyphenylene oxide (PPO) particles as a toughening agent in a Cytec 5250 BMI system comprised of BDM, DABA and 2,4-bismaleimidotoluene, another important commercial monomer [91]. They were able to increase the fracture toughness of the system from 0.97 to 1.40 MPa $m^{1/2}$ without altering its T_g, which was maintained at 275 °C. The disadvantage to this method is the increase in viscosity associated with the addition of particle fillers. Particle toughening has also been shown to increase the compression after impact performance of BMI resins, with 60 MPa improvements being obtained [78].

The introduction of thermoplastic particles and associated interleaf toughening in composite prepreg systems will continue to form the backbone of commercial toughened aerospace polymer systems. Significant improvements have already been achieved with toughened epoxy prepreg systems, and these tend to act as pathfinders for the application of similar technologies to other high performance polymers.

4. THERMOSET BLENDS

The combination of BMIs with other high performance thermosets can enable their good elevated temperature performance to be exploited in tandem with the advantages offered by the secondary system. Following judicious choice of stoichiometries and processing conditions, it is possible to produce copolymers or interpenetrating networks that outperform both of their constituent homopolymers for a desired application. Many of these blended systems have also been subjected to similar modifications as the neat BMI resins, including the use of thermoplastic or nanofiller additives [92].

4.1 BMI/Epoxy

Epoxy resins are the dominant polymers in the advanced composites industry, particularly in the commercial aerospace sector. Their high performance characteristics combined with excellent processability have enabled them to attain an insurmountable position as the leading matrix resin for widespread applications [93]. However, conventional epoxies are limited by their relatively low glass transition temperatures (resulting from poor hot/wet performance), meaning that they can only safely be used at temperatures up to around 140 °C. Conversely, BMIs are able to withstand higher temperature environments but suffer from their processability. It has therefore been suggested that the combination of the two systems will lead to a material that exhibits the beneficial characteristics of the two constituents.

There are a number of different pathways through which these two materials can co-react to form a single three dimensional network thanks to the varied reactivity of the two functional groups of interest; epoxies and maleimides. For example, an epoxy component can be added to the widely used BDM/DABA system [94]. The nucleophilic hydroxyl groups on the DABA molecules are able to form covalent bonds with epoxide groups through a nucleophilic addition/ring opening reaction. Conversely, a BMI can be mixed in with a typical epoxy/diamine resin, where it can react with the crosslinking agent via Michael addition [95]. The latter system yields thermosets with high T_g (> 250 °C), reduced moisture absorption and liquid processability. More recently, BMI/epoxy blends have been suggested as a suitable matrix for fabricating rigid risers for oil and gas rigs *via* filament winding [96]. While promising, there are still issues that need to be addressed for this application, such as the potential galvanic corrosion of these carbon fibre based composites in deep sea environments, an issue not addressed at all in the publication despite the known weakness of BMIs in this area [97].

4.2 BMI/Cyanate Ester

BMIs have been blended with cyanate esters to produce substrate materials for printed circuit boards (PCBs), an industry that is responsible for a large proportion of BMI consumption. The combination of these thermosets are commonly known as bismaleimide-triazine, or BT, resins. These systems were first produced by the Mitsubishi Gas Chemical Company in 1978, with the intention of combining the low dielectric constant and good moisture resistance of cyanate esters with the high temperature stability of BMIs [98]. Traditionally, this market has been dominated by flame resistant epoxy resins, specifically a material known commercially as FR-4 (based on tetrabromodiglycidyl ether of bisphenol A), and the technology is now extremely well established. However, the drive for more advanced electronics has led to a demand for circuits with higher densities and powers whilst operating at higher temperatures and with more stringent insulation resistance and low cross talk requirements [99].

There has been some debate as to the nature of the curing reactions taking place in the blend of cyanate esters with BMIs. Some researchers believe that the two networks react independently of one another to form an interpenetrating polymer network (IPN). This theory is backed up by the fact that the cured BT resins often exhibit two distinct glass transitions, which is what would be expected for a material containing two different polymer networks [100]. Additionally, the ^{15}N-NMR spectrum of a model system revealed no evidence of a co-polymerisation reaction [101]. Alternatively, it has been suggested that the two different monomer species are able to co-react to form pyrimidine and pyridine linkages (Figure 22) and hence a single network [102]. This hypothesis has been supported by FTIR and ^{13}C-NMR spectra indicating the existence of these products. An investigation by Lin *et al.* in 2004 suggested that the nature of the network formed is highly dependent on the presence or absence of a catalyst in the system [103]. These catalysts promote the cyclotrimerisation of the cyanate ester linkages, and thus if they are present the CE and BMI molecules react independently. Lin *et al.* postulate that with no catalyst present, the two species cross react, although this is also disputed. More recently, the role of organic solvents in commercial BT resins has been explored to determine the roles of each in terms of solvation or promotion of homopolymerisation reactions; no evidence of BMI/cyanate ester co-reaction was found [104]. Co-reaction between the two systems can be ensured by adding molecules containing dual functionality capable of reacting with both blend components, such as *p*-cyanatophenylmaleimide, thus enabling inter-system crosslinking [105].

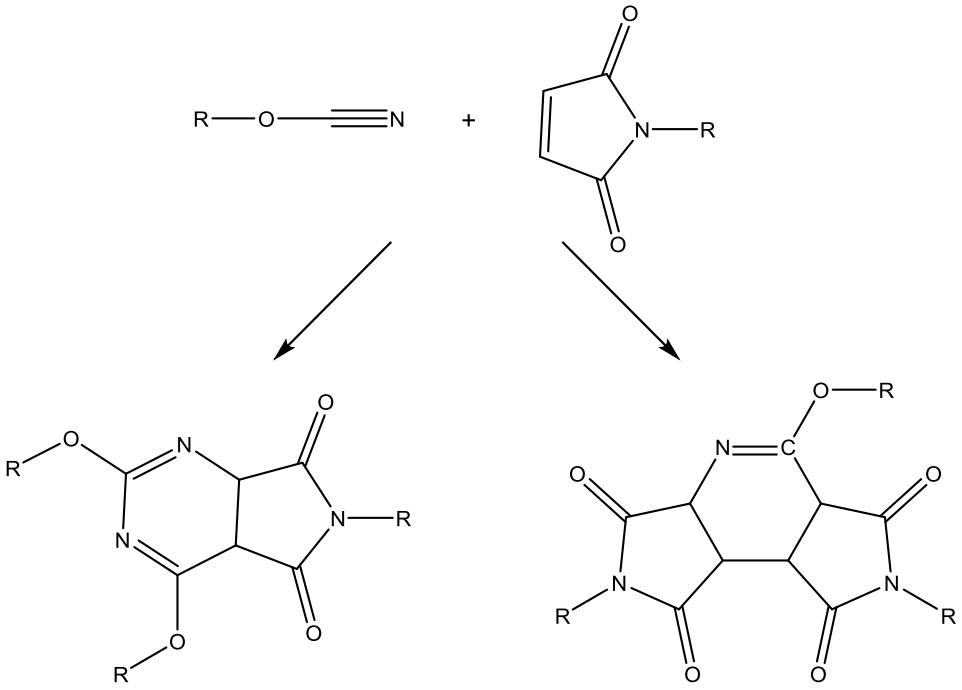


Figure 22: Reaction schemes which have been proposed for the co-reaction between BMI and CE monomers.

One drawback associated with the use of BT resins is their poor processability. At present, a mixture of high boiling point solvents is required in order to dissolve the monomers and reduce the blend viscosity. These solvents include *N*,*N*-dimethylformamide, *N*-methylpyrrolidone and *N*,*N*-dimethyl acetamide, which are potentially harmful to end users and the environment upon disposal. Recently, researchers have investigated novel methods of improving upon this aspect of BT systems. One strategy that has been attempted is the use of bulky pendant groups and unsymmetrical structures to lower monomer melting points and improve solubility in more conventional industrial solvents [51]. Another idea is the use of liquid cyanate ester monomers to dissolve the BMI components and hence produce a liquid processable system without the need for additional solvents [106]. Initial results have been successful, with liquid processable systems capable of producing high T_g materials; however, more work is needed in this area.

Work by Hamerton *et al*. showed that BMI/CE blends can be susceptible to significant water uptake if exposed to humid environments for extended periods of time, with the blends absorbing more water than either of the homopolymers [107]. This was investigated by conditioning samples in 70°C water for 14-17 months, and led to severe blistering or cracking in some samples. The problem worsens as the content of BMI in the system is increased, however it can be somewhat

ameliorated by incorporating allyl containing CE monomers into the blend, with dramatic reductions in moisture uptake (5 – 9 % compared to 7 – 22 %) being achieved [108].

4.3 BMI/Benzoxazine

Polybenzoxazines (PBZ) are a novel class of high performance polymer that have garnered significant interest in recent years due to their broad range of outstanding and unique properties [109]. These include high T_g, chemical resistance, low moisture absorption, minimal shrinkage, thermal stability and low dielectric constant. There is also great scope for polymer tailoring due to the flexibility of monomer design and synthesis. However, as is the case with most thermosetting polymers, there are issues including cure times/temperatures and brittleness. Additionally, while the T_g of the materials is typically able to compete with epoxies, it is not high enough for more advanced high-temperature applications. This has led to a number of investigations into the combination of BZ monomers with BMIs, in order to improve the temperature performance and processability of benzoxazine while maintaining its beneficial properties. Interestingly, it has been observed that the blending of these two components leads to a lowering of the BMI cure temperature, suggesting that BZ is able to catalyse its cure. It has been speculated as to the exact catalytic mechanism, with some suggesting that it arises due to the presence of amine groups in reacted benzoxazine, while others suggest that the iminium ions formed as the benzoxazine ring opens could be responsible.

Kumar *et al*. looked at cured BZ/BMI blends under scanning electron microscopy (SEM) and discovered evidence of micro-phase separation between the two components of the system [110]. In an effort to produce a more homogenous thermoset, they synthesised a BZ monomer containing two allyl groups (Figure 23) in the hope that it might react with BMI in the same way as DABA, thus covalently linking the two interpenetrating networks. This proved to be a success, with DSC and IR both indicating the occurrence of the expected ‘Alder-ene’ type reaction. There were also indications of hydrogen bonding between the carbonyl groups of BMI and the hydroxyl groups from BZ. However, it was found that the glass transition temperature of the blend (T_g = 274 °C) was lower than that of both individual monomers, suggesting that the degree of crosslinking attained from the copolymer is lower. Conversely, Wang *et al*. combined the same BZ-allyl molecule with a different BMI monomer and found that large increases in impact strength (from 6.1 to 11.8 kJ m^{-2}) and reductions in dielectric constant (3.10 to 2.96 at 60 Hz) could be achieved (compared to the neat BMI) with only a small cost in terms of thermal performance and stability [111].

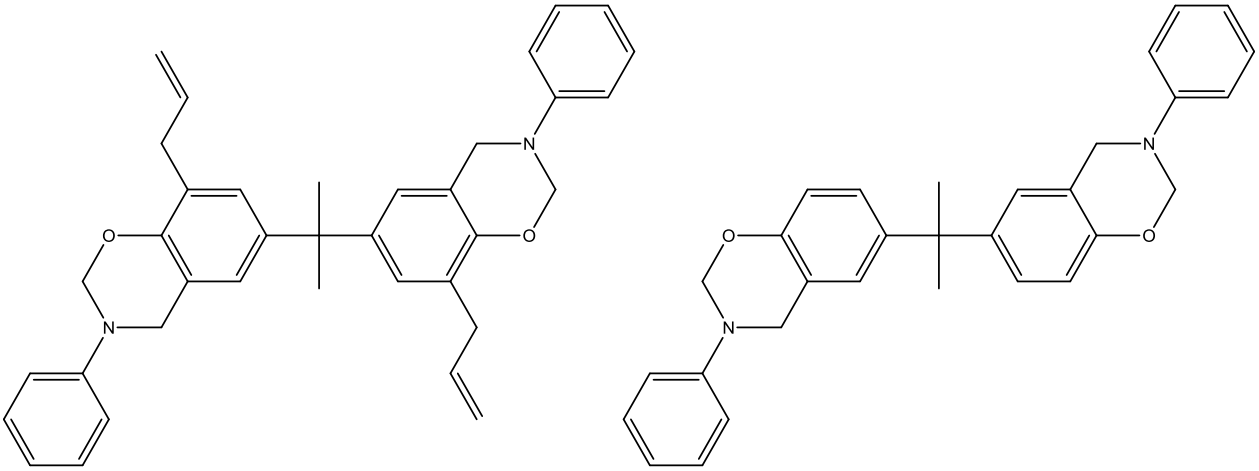


Figure 23: Examples of benzoxazine monomers diallyl BA-a (left) and BA-a (right) that have been used to modify BMIs.

There are several examples in which the BZ/BMI combination has been claimed to lead to improvements compared to both homopolymers [112,113]. These improvements are not just in terms of mechanical properties such as impact strength and flexural strength, but also in terms of glass transition temperature. Such blends have been successfully used to impregnate reinforcing fibres to produce a new family of composite materials. This makes these blends highly attractive for a range of high performance applications, from aero structures through to printed circuit board substrates, and as such there are now examples of patented BZ/BMI blends [114].

Another way to overcome microphase separation between BZ and BMI is to synthesise a monomer that contains both functionalities. This idea has been reported by Jin *et al.* [115], who fabricated a series of bis(benzoxazine-maleimide)s (Figure 24) as a novel class of advanced thermoset. The polymers produced possessed good thermal properties (T_g in the range of 289-307°C), with the monomers being readily soluble in a range of common organic solvents, thus giving them potential for easy processing. So far, there has been no published work detailing the mechanical or dielectric performance of these materials.

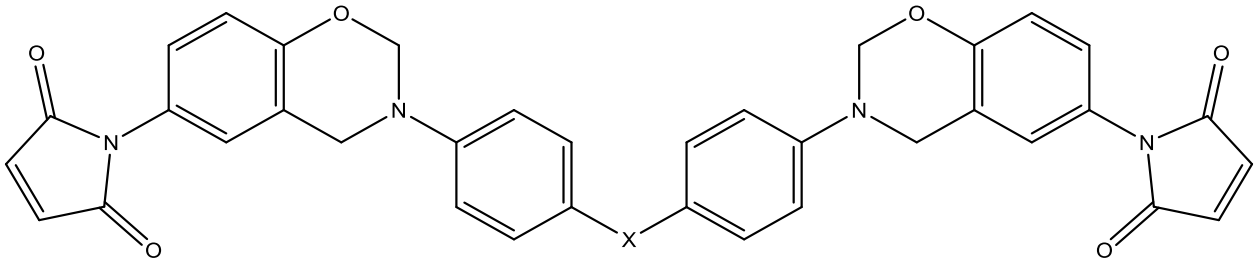


Figure 24: Monomer containing both BZ and BMI functionalities.

The concept of applying multiple thermosetting functionalities in the same molecule was also adopted by Gao *et al*., who produced a molecule containing maleimide, benzoxazine and acetylene functionalities (Figure 25) [116]. The polymer produced exhibited a T_g over 300 °C, a thermal degradation temperature over 400 °C and a very impressive 800 °C char yield of 61.2 %, however no mechanical properties were reported. It should also be noted that these molecules can require complicated syntheses, making them less attractive to industry.

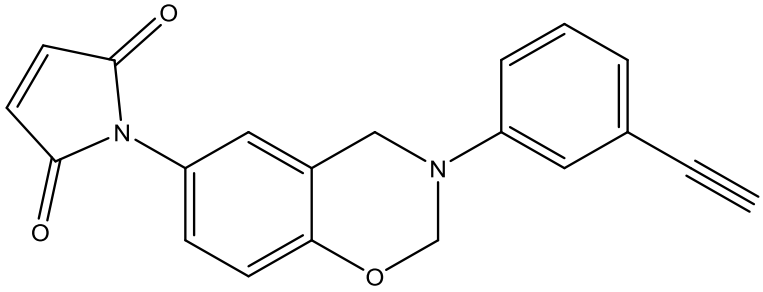


Figure 25: Monomer containing three different thermosetting functionalities.

4.4 Ternary blends

Thanks to the ever-expanding range of thermoset materials classes, there are now opportunities to explore more complex multi-component blends, several of which have been investigated. The aim of ternary thermoset blends is to combine the advantageous properties of three different monomers. When BMI monomers are included in such systems, they are used with the intention of improving the high temperature properties of the terpolymer. Epoxy resins have been added to BMI/CE blends to try and improve the toughness and processability of the system [117]. It was found that the impact strength increased by 1.46 times to 13.5 kJ m^{-2} when 20 wt% of epoxy was incorporated. Whilst there was only a 7 K drop in T_g, both the thermal degradation temperature and dielectric constant were adversely affected (by 21 K and 0.25 respectively). An alternative system replaced this epoxy with bis allyl benzoxazine, leading to improvements in all of the measured properties including T_g, impact strength, dielectric constant and moisture resistance compared to the neat BMI/CE blend [118]. The claimed properties make the material attractive for PCB substrate application. Similarly, a patent has been taken out on a blend of BMI, benzoxazine and epoxy for use as a high temperature adhesive in electronic applications [119].

This is an area that will inevitably grow along with the need to maximise the final properties achieved with existing polymers in the form of non-reactive blends (to form IPNs) and true copolymers. The story of the development of BMIs (and particularly the reduction in the rate of production of new BMI monomers) exemplifies this.

5. NOVEL BMI NANOCOMPOSITES

The discovery and development of nanoscale materials with outstanding mechanical properties, such as carbon nanotubes and graphene, has led to significant efforts to incorporate them as reinforcement materials in polymer matrices. To this end, researchers have investigated the used of nanoscopic fillers in BMIs in order to improve toughness, as well as producing processable materials with excellent mechanical properties at high temperatures.

5.1 Carbon Nanotubes

Functionalised carbon nanotubes (CNTs) have been incorporated as the reinforcement material in BMI resin systems, enabling the production of composites with excellent mechanical properties. The performance of these composites has been found to be highly dependent on both the degree of alignment and surface functionalisation of the carbon nanotubes. Initial investigations into composites of this type showed much lower properties than those predicted thanks to poor control over nanotube alignment, low CNT loadings and weak interfacial interactions between reinforcement and matrix. In 2009, Liang *et al.* investigated using a simple method of mechanical stretching followed by resin impregnation in order to produce CNT-BMI composites with a high degree of nanotube alignment [120]. This also helped to overcome the issue of low CNT loading, hence increasing the final properties further. It was found that both the tensile strength and modulus of the composite could be significantly improved by aligning the nanotubes using the stretch method, with both properties increasing by a factor of four compared to the same material with randomly orientated nanotubes to a maximum of 2088 MPa and 169 GPa respectively. These properties are comparable with state of the art continuous fibre composites. The glass transition temperature of the produced material was over 250°C, and the alignment of the fibres also led to large increases in the electrical conductivity of the composite.

These high mechanical properties were further improved by changing the nature of the interfacial adhesion between the matrix and reinforcement. The interfacial bonding between a carbon nanotube and a matrix resin is typically poor due to the atomically smooth surface of the nanotubes [121]; however, it is possible to functionalise the surface of the nanotubes to introduce groups that can react with the curing resin to form strong covalent bonds. The downside to this functionalisation is that it often leads to degradation in the mechanical and electrical performance of the nanotubes as the delocalised π system is disrupted. Peroxy acids can be used to introduce epoxide rings to the surface of a carbon nanotube, as shown in Figure 26, which can then react with the DABA component of a BMI blend and thus form covalent bonds between the nanotube surface and the polymer network.

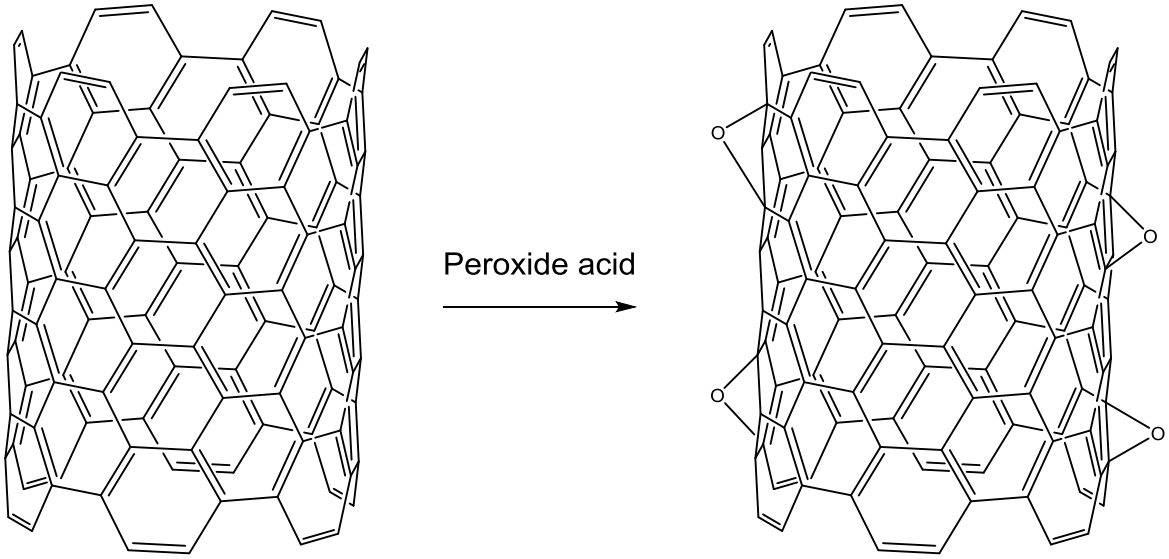


Figure 26: Surface Functionalisation of carbon nanotubes.

This led to the production of nanocomposites with unprecedented mechanical performance: a Young's modulus of 350 GPa and tensile strength of 3081 MPa vastly exceeding the properties of conventional composites [122]. The functionalisation of nanotubes led to losses in terms of the thermal and electrical performance of the materials, with both T_g and conductivity decreasing. The loss in conductivity can be partially accounted for by using nanotubes of a longer length, whilst having little to no impact on the mechanical performance [123]. CNTs have also been shown to have an impact on the toughness of BMI resin systems, which is important as their brittleness is one of the major drawbacks to these materials [124]. The incorporation of 0.5 wt% of CNTs treated with MDA was responsible for a 60 % improvement in the impact strength of a BMI resin, with no decrease in thermal performance.

5.2 Graphene

Graphene, discovered at the University of Manchester in 2004 [125], is a two dimensional allotrope of carbon consisting of just a single graphitic layer (Figure 27). It possesses some remarkable properties including exceedingly high stiffness and near zero resistivity. As the synthesis and production of graphene has developed, there has been a drive to utilise this latest 'wonder material' in composite materials to further refine their properties. This includes the modification of BMI resins with the nanomaterial.

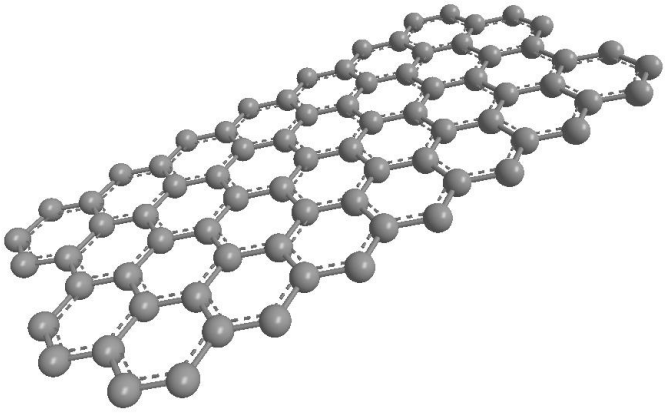


Figure 27: The structure of graphene.

Researchers have reported that the inclusion of low weight percentages (≈1 wt%) of graphene oxide, the oxidised version of graphene that exhibits better processing characteristics, but significantly poorer conductivity, can lead to enhancements in impact strength of 37 % [126,127]. The use of a nanofiller in this regard is advantageous as it does not reduce the degree of crosslinking of the resin so should not impact upon its thermal performance. Indeed, the thermal degradation of the studied BMIs has shown to be unaffected by the addition of graphene oxide, although the glass transition temperatures of the materials have not been investigated or reported. Additionally, it is unknown as to how graphenes inclusion might impact upon the processability of the resin in terms of increased viscosity. Further studies have shown that, in a similar manner to CNTS, that surface functionalisation of the graphene filler has a significant effect on the material properties obtained [128]. Functionalising reduced graphene oxide (RGO) with hyperbranched polytriazine via a silane treatment led to an increase in resin impact strength of 70 % compared to the same resin filled with unfunctionalised RGO.

5.3 Boron Nitride

Boron nitride is another nanomaterial that exhibits interesting properties that may be suited to application in polymer composites. Its excellent thermal conductivity has led to attempts to incorporate these materials into BMIs order to improve their ability to dissipate heat, particularly for higher temperature applications. In 2013, Zeng *et al*. prepared BT resins filled with hexagonal boron nitride [129]. The addition of 50 wt% boron nitride filler to the BT resin was shown to increase its thermal conductivity by almost an order of magnitude to 1.11 W/mK. It is thought that this could be improved further by using higher quality filler material. When there is a sufficient content of BN, the particles contact with one another to form a continuous network through which heat is readily conducted. There is also an increase in the thermal degradation temperature.

However, these improvements are offset by a drop of 34 K in the T_g and an increased dielectric constant (4.5 compared to 3.3 for the neat resin).

5.4 POSS reagents

Polyhedral oligomeric silsesquioxane (POSS) reagents (Figure 28) have attracted interest in the field of BMI/CE blends because of their low dielectric constants (typically 2.1-2.8) and ability to be functionalised, thus forming an organic shell capable of co-reacting with thermosets. They are also thermally stable and resistant to oxidation. It is therefore anticipated that they may be able to improve the performance of these systems for PCB applications. Hydrogen silsesquioxane, the most basic POSS reagent, was used to improve the T_g and thermal stability of BDM/DABA, with T_g increasing by 20 K upon the addition of less than 10 wt% of the POSS reagent [130] Changes in the

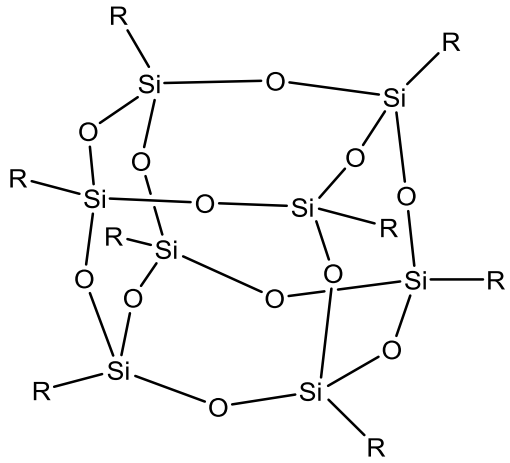


Figure 28: The general structure of the most common form of POSS reagent, where R is commonly a branched alkyl chain *e.g.* isooctyl or isobutyl with one or more R groups replaced with a reactive functional group).

mechanical performance of this system are unreported. In 2008, Cao *et al*. synthesised a maleimide functionalised POSS derivative dubbed octa(maleimidophenyl)silsesquioxane and incorporated it into a BMI/CE system [131]. At low weight percentages (1-2 %) there was a marked reduction in the materials dielectric constant (from 3.7 to 3.0) with minimal change in thermal performance in terms of both T_g and thermal degradation temperature. The same modifier was also investigated in a standard BDM/DABA system and led to improvements in processability, leading to a system with a low viscosity (3 Pa s) from 90 °C up to 190 °C [132]. However, the synthesis of this modifier was highly complex and the network produced was particularly brittle. An alternative POSS molecule containing aminopropyl substituents was proposed, with the primary amino group capable of interacting with both BMI and CE resin constituents [133]. Again, improved dielectric properties

were obtained. A further aryl-amine derivative was incorporated into a series of linear aliphatic ether linked BMIs resulting in improvements in T_g, thermal stability and dielectric properties compared to the neat systems [134].

5.5 Nanoclay fillers

Polymer-clay nanocomposites were initially developed using thermoplastic matrices such as polyamides, but have since been investigated using thermoset resins. Meng and Hu added two commercial nanoclays to a BDM/DABA system and found that, using the appropriate preparation and exfoliation conditions, this could increase the impact resistance of the cured resin twofold [135]. A similar experiment utilised organic rectorite as the nanofiller, wherein the clay is ideally fully exfoliated to allow intimate mixing of the BMI with the clay prior to thermal cure (Figure 29) [136].

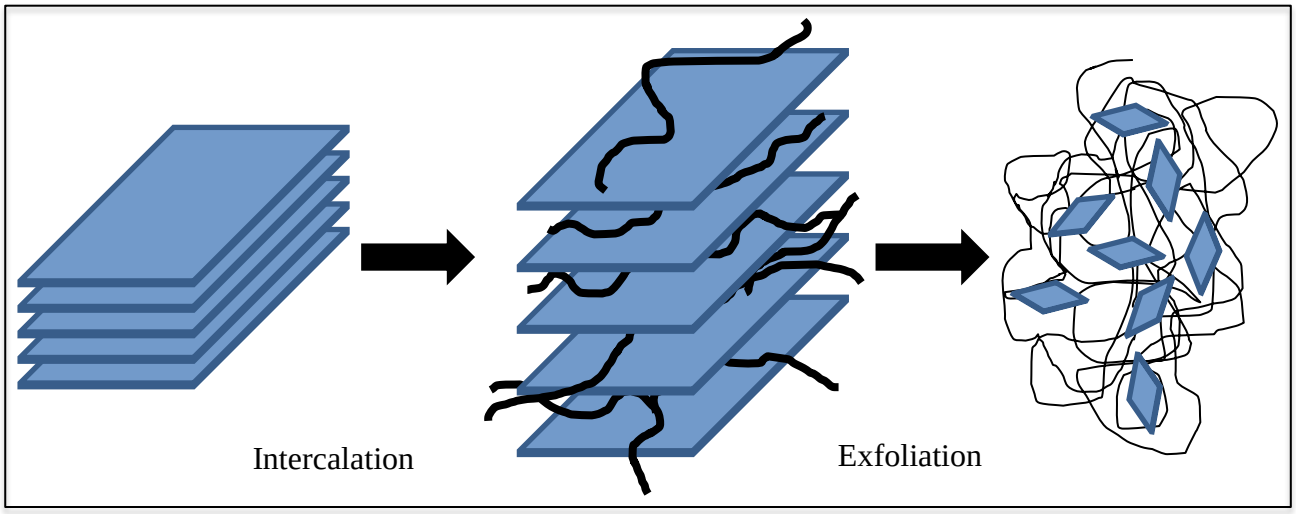


Figure 29: Schematic of rectorite and the process of exfoliation

This system also exhibited improved impact resistance, albeit a more moderate improvement of 30 %, with limited negative effects in terms of T_g and thermal degradation temperatures. Furthermore, the water resistance of the resin was slightly increased, and it has since been used to successfully fabricate glass fibre composite specimens [137]. Modified montmorillonite is another nanoclay that has been used in BMI systems, in this instance being used to improve the properties of BT resin [138]. The addition of 5 wt% of this material to the system led to improvements in a number of key properties including impact strength (8.2 to 15.7 kJ m^{-2}) and dielectric constant (3.45 to 3.25 at 10^6 Hz), as well as modest improvements in T_g and T_d.

5.6 Nanosilica

Nanosilica is another nanomaterial that has been investigated in the context of bismaleimide reinforcement. Nelson *et al.* produced nanosilica filled BMI resins with the intention of improving mechanical properties to enable the production of superior composite tooling [139]. Of particular concern for this application are coefficient of thermal expansion (CTE), shrinkage and hardness. They found that by using 40 wt% of silica particles they were able to improve all of these aspects, with CTE decreasing from 40 to 24 μm/m/°C, shrinkage decreasing from 0.66 to 0.33 % and indentation hardness doubling from 0.3 to 0.6 GPa. Furthermore, fracture toughness was doubled and T_g was maintained, however there was an associated increase in the materials viscosity. Yuan *et al.* used nanosilica in a BT resin to improve its dielectric properties [140]. They were able to achieve a moderate reduction in both dielectric constant and loss. As with previously mentioned nano-reinforcements, it has also been shown that control of the chemistry at the nanosilica surface can lead to improvements in properties [141]. In this case, the introduction of maleimide or amine groups to the particle surface lead to increases in T_g (up to 15 °C) and reductions in CTE (up to 8 °C/ppm) compared to unmodified particles.

The explosion in the interest in nanocomposites, particularly where carbon nanotubes or graphene are involved, mirrors the increasing drive to develop truly multifunctional polymer blends and composites (in which enhancements in *e.g.* electrical or thermal conductivity can be realised). The topic will grow and broaden, particularly in the field of BMIs, but the challenge of producing well-dispersed formulations will be key to maximising their potential.

6 BMIs IN SMART MATERIALS

6.1 Shape memory polymers based on BMIs

Recently, attention has turned to the possibility of utilising the high temperature performance of BMIs in order to fabricate new shape memory polymers (SMPs). These are materials capable of recovering their original shape after being deformed upon the application of a stimulus, typically heat or light, giving the potential to produce reconfigurable structures. The challenge associated with the development of such materials, particularly in an aerospace environment, is the balancing of a large, reversible strain capability, high activation temperature and sufficient mechanical properties. In 2012, McClung *et al*. investigated a BMI based SMP consisting of BDM, an aliphatic diamine and a bis-isocyanate as a crosslinking agent (Figure 30) [142]. They were able to produce materials with transition temperatures ranging from 110 to 164 °C capable of recovering their initial shape after 30 seconds at the required temperature. These transition temperatures proved to be higher than those of commercially available SMPs Veriflex and Veriflex-E, which undergo T_g at 84

and 100 °C respectively [143]. Similarly high transition temperatures have also been achieved by using vinyl monomers as the BMI co-monomer [144].

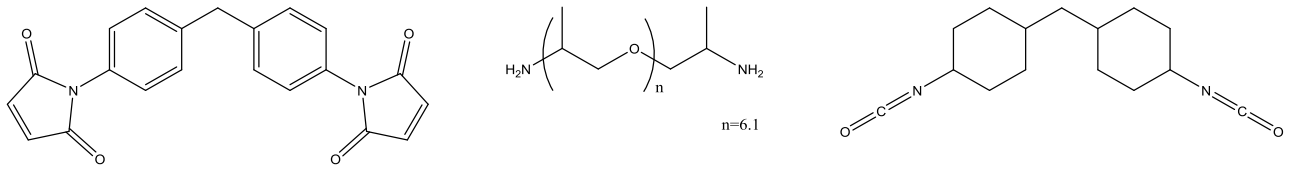


Figure 30: Components of the BMI based shape memory polymer

An alternative SMP has been prepared by Biju and Nair using BMPP, DABA and bismaleimide-end-capped poly(tetramethyleneoxide) (dubbed PTMO) [145]. They were able to obtain polymers with transition temperatures as high as 220 °C. It was noted that superior mechanical properties and higher transition temperatures were obtained for lower PTMO contents, but this also coincided with an increase in shape recovery time.

6.2 Bismaleimides in self-healing thermosets

Self-healing materials are attractive as they have the potential to increase the durability and safety of a component. In the event of fracture, such a material is able to reform its three-dimensional network and hence maintain its mechanical performance. Bismaleimide chemistry has been exploited in this field thanks to its ability to undergo reversible Diels-Alder reactions, as outlined in Figure 31.

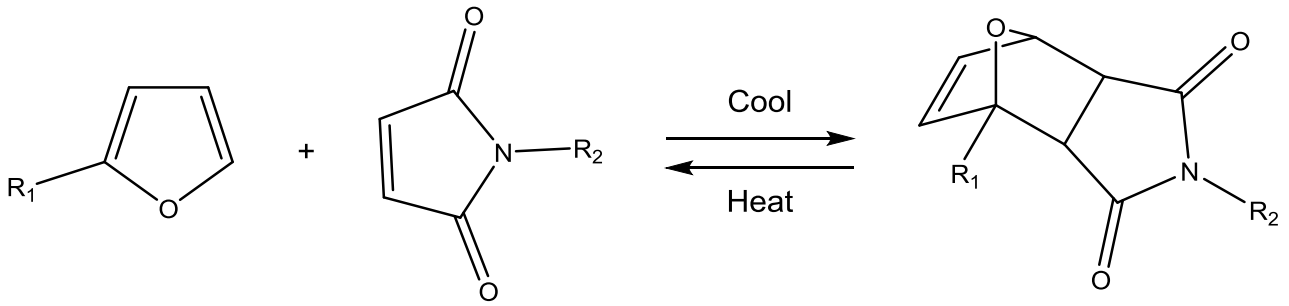


Figure 31: The reversible Diels-Alder reaction between furan and maleimide.

Peterson *et al*. functionalised an epoxy network with furan moieties capable of undergoing such a reaction with maleimide groups [146]. Once the material had fractured, a BDM in DMF solution was injected into the crack, and left to undergo Diels-Alder addition reactions with these furan groups at room temperature and hence heal the crack. It was found that healing efficiencies of 70 % could readily be achieved with concentrated BMI solutions. However, it must be noted that the healing is limited to low temperature systems, as the retro-Diels-Alder reaction occurs at 90 °C,

meaning that the healed network decomposes at this temperature. The same chemistry was employed by Scheltjens *et al*. who incorporated both BMI and furan containing components into the same network [147]. They found that the network could be healed upon heating and cooling, and suggested that such a polymer could find use as a self-healing coating. Similarly, the incorporation of the two reactive groups mentioned into a linear polyurethane rather than a crosslinked epoxy enabled the production of a polymer with healing efficiencies up to 80 % [148]. In a further study, the BMI molecules were used as a sizing on both carbon and glass fibres to enable thermally initiated healing of the fibre resin interface upon debonding [149]. A healing efficiency of 82% was obtained. The self-healing potential of BMIs has also been combined with nanocomposite technology. Xu *et al.* demonstrated that it is possible to functionalise a POSS molecule with furan groups via an epoxide-containing intermediate [150]. This material was capable of undergoing crack healing at 135 – 150 °C, however it was noted that scratches on such a material could not be replenished due to the removal of necessary material.

The growing interest in multifunctional 'smart' polymers has already been mentioned, but BMIs have already featured in several studies in which the high performance characteristics of the polymer and the value of the monomer make the self-healing approach worthy of further examination to restore value and extend their life. Recently, BMI chemistry has been applied to other multifunctional polymer concepts, having been used in tandem with divinylbenzene in the production of microporous polymers for use in gas storage and heterogeneous catalysis [151].

7. CONTINUOUS FIBRE BMI COMPOSITES

BMI resin systems designed for use in continuous fibre composites are now commercially available from numerous suppliers including Cytec, Hexcel, Evonik, TenCate, Renegade Materials Corp and Raptor Resins [6]. Applications are generally limited to those exposed to high temperatures where strong hot/wet performance is required, such as in space structures, military aircraft and composite tooling. While BMIs are primarily used to produce prepreg materials for autoclave processing, the field has significantly advanced with the introduction of out-of-autoclave resins, as well as those designed for resin transfer moulding (RTM) [152-154]. In order to enable these materials to be produced on large scale, other modifications to the resin systems needed to be introduced for processing rather than performance purposes.

The pot-life of a thermosetting resin is an important consideration when developing successful commercial materials. Over time, a thermosetting resin slowly cures even at low temperatures, leading to pressures on manufacturing timescales. A longer shelf life is useful in ensuring that the

resin does not lose its processability or performance characteristics. It is also important that the resin can be handled at elevated temperatures without immediate curing for techniques such as RTM. In the case of BMIs, it has been found that it is possible to extend the pot-life by adding free radical inhibitors to the resin mixture [155]. These inhibitors include readily available molecules such as hydroquinone or naphthoquinone, and are able to improve the storage stability whilst having minimal impact on the mechanical performance of the resin produced. The disadvantage of this method is that it can mean that higher temperatures or longer cure times are required to overcome the inhibitors effect; the use of inhibitors can cause a trade-off between pot life and curing efficiency.

Another processability problem associated with BMI resins is the fact that they often suffer from excessive flow, which can lead to part quality issues. It has been found that it is possible to stabilise the flow properties by the addition of high molecular weight elastomers to the resin blend. Examples of polymers include poly(ethylene oxide) and polybutadiene/PAN copolymers, typically with molecular weights of around 2,000,000 g mol^{-1}. The addition of a very low weight percentage of such a polymer (*ca.* 1 wt%) is sufficient to provide the necessary improvements in resin flow and thus enable the production of effective BMI prepregs [77].

The application of BMIs to advanced composites (particularly military aerospace) is key to the future success of this family of polymers, since the present cost renders them applicable to only relatively minor niche areas in civil aerospace for which they are typically over engineered. A review of the application of BMIs in modern composite technology and structural engineering falls outside of the scope of this review, with its focus on polymer science, but this is currently receiving our attention.

8. CONCLUSIONS AND FUTURE OUTLOOK FOR BMI CHEMISTRY

Since the initial emergence of BMI resins as competitive high performance systems, there has been great interest in harnessing their unique combination of high temperature performance and good processability. During the 1980s, a number of international research groups in academia concentrated on using the synthetic chemistry available to develop a large range of aliphatic and predominantly aromatic BMI building blocks based on many of the diamine intermediates that feature in epoxy resin chemistry. The predictions at the end of the decade suggested a growth in the adoption of BMIs in the aerospace composites industry. However, in common with several other families of high performance thermosets the 1990s saw a dramatic contraction in the number of published synthetic studies in this area and a rationalisation of the range of commercial resins

available. Now, in the second decade of the 21st century the portfolio of commercial BMIs is largely based on fewer than half a dozen monomers in combination with selected diamine and allyl substituted bisphenols. The technology has matured to such a level that commercially available systems are being considered for advanced applications, thanks mainly to the advances made in the ability to toughen the thermoset. One of the main barriers to widespread acceptance and adoption of BMIs has been the perception of toxicity associated with the use of MDA, or the presence of residual MDA in the blend. The development of commercial BMI products has concentrated on their refinement to achieve significant reductions in residual MDA or the use of alternative, less toxic precursors. The other major obstacle in BMI uptake has been the high cost of materials relative to the industry standard epoxies, limiting their use to specialist high performance applications. In common with many other competing resin families, new developments tend now to concentrate on the incorporation of well-dispersed additives and nano-fillers in order to enhance cured BMI properties, rather than exhaustive synthetic programmes.

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